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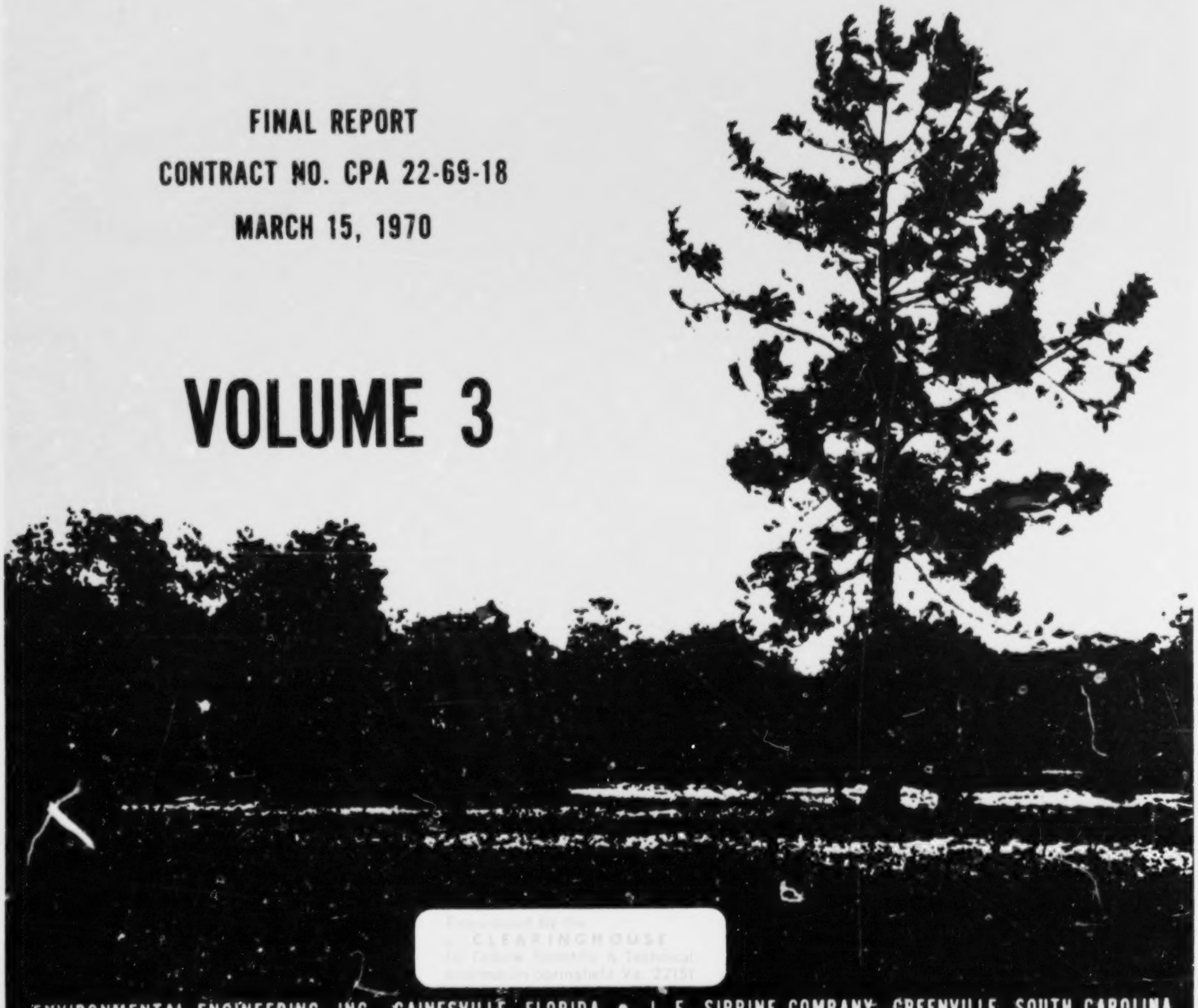
CONSUMER PROTECTION AND ENVIRONMENTAL HEALTH SERVICE
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
DIVISION OF PROCESS CONTROL ENGINEERING
DIVISION OF ECONOMIC EFFECTS RESEARCH

CONTROL OF ATMOSPHERIC EMISSIONS IN THE WOOD PULPING INDUSTRY

FINAL REPORT
CONTRACT NO. CPA 22-69-18
MARCH 15, 1970

VOLUME 3



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VOLUME 3

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CHAPTER 9

SAMPLING AND ANALYTICAL TECHNIQUES

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CHAPTER 9

SAMPLING AND ANALYTICAL TECHNIQUES

SUMMARY

At the very heart of any program to improve air quality are adequate and accurate sampling and analytical techniques. Monitoring of both the ambient air and sources of emissions are necessary to define the problems, determine the basis for design of corrective measures, if necessary, and evaluate the results of reducing emissions. Both sampling and analysis are equally important parts of the monitoring procedures.

This chapter is not intended as a complete description of all sampling and analytical techniques applicable to pulping operations. The references cited, however, do give complete details. Most of the methods applicable to both sources in the mills and the ambient air must be considered research methods in a state of evolution at this time. Few standardized procedures are available at present for the compounds of interest. Information on accuracy, precision, and reliability is very limited.

The sampling and analysis of gases and particulates produced during the manufacture of pulp, whether they be in the emission streams or in the atmosphere, has been in a rapidly changing state as the result of continuing application of new technology. The last twenty years has seen progress from the early applications of conventional wet chemical analytical techniques to the development of relatively sophisticated gas chromatographic procedures which permit sulfur-specific separation of a spectrum of sulfur-containing compounds present in the atmosphere and in the pulping process emission streams and final reduction of the analytical data by computer from data logged on magnetic tape. Each of the various available analytical procedures has either served a useful purpose in providing

initial identification of the type and magnitude of the pulping industry's air pollution problem or in the immediate and continuous monitoring and control of the unit processes so that the causes of the emissions can be minimized or eliminated.

It must be recognized that suitable methods of analysis are not available for all compounds of interest. A review of the avaliable methods for malodorous sulfur compounds reveals that many are inadequate or relatively new and untried. It is apparent that many of the available methods and instruments have not achieved the state of reliability and simplicity needed for routine application.

The descriptions and evaluation of available methods are grouped under source or ambient for each of the pulping processes of interest to this study (kraft, sulfite, and NSSC). For each grouping recommendations are made of the best available procedures.

9.1 INTRODUCTION

At the very heart of any program to improve air quality are adequate and accurate sampling and analytical techniques. Monitoring of both the ambient air and sources of emissions are necessary to define the problems, determine the basis for design of corrective measures if necessary, and evaluate the results of reducing emissions. Both sampling and analysis are equally important parts of the monitoring procedures.

This chapter is not intended as a complete description of all sampling and analytical techniques applicable to pulping operations. The references cited, however, do give complete details. Most of the methods applicable to both sources in the mills and the ambient air must be considered research methods in a state of evolution at this time. Few standardized procedures are available at present for the compounds of interest. Information on accuracy, precision, and reliability is very limited.

9.1.1 GENERAL PROBLEMS OF SOURCE SAMPLING

Collection of representative samples of gases and particulates from a source is an art in itself. Separation of particulates and gases from the gas stream is frequently required and presents special problems in this instance because of the possibility of odorous gases being adsorbed on the particulates.

The sampling of particulates requires that strict attention be given to the well known problems associated with isokinetic sampling. When particulate matter is in the range of 3 μ or greater, the inertial effect on the particles can produce an erroneous sample if the velocity of the sample in the sample nozzle or probe is not the same as the velocity of the gas stream at the sampling point. When the gas velocity within the probe is less than the gas velocity in the duct, the sample collected contains a relatively higher proportion of heavier particles and the error is on the high side. Conversely, when the sample gas velocity is greater than the gas velocity of the duct, the heavier particles are not collected, and the error is on the low side.

It has been concluded from many isokinesic studies reported in the literature that isokinetic sampling is not necessary when the particulate matter sampled is below 5 μ in size.

Procedures and recommendations for conducting source sampling have been published by the National Council for Air and Stream Improvement (67, 74), Industrial Gas Cleaning Institute (71 - 73), and American Society of Mechanical Engineers (66).

Several extensive research contracts on source sampling are being conducted for NAPCA. Results of these studies should improve our knowledge concerning source sampling techniques.

9.1.2 GENERAL PROBLEMS OF AMBIENT SAMPLING

There are several stages involved in making quantitative determinations of the relatively low concentrations of gases and particulates of interest in the ambient air. Representative samples must be collected, refined, and analyzed before results can be calculated. Decisions must be made as to location of collector, type of collector, size of sample required, rate and duration of sampling, and analytical technique to be used. Such decisions frequently are not mutually independent. The problems associated with separation of gases and particulates are of importance for the reasons cited in the last section.

Procedures for planning the sampling of the atmosphere are available from NCASI, ASTM, APCA, and the Intersociety Committee.

Unfortunately few standard methods of analysis with known precision, accuracy, and interferences are available at this time for compounds of interest. Hopefully the activities of the Intersociety Committee, ASTM, and the Analytical Methods Evaluation Service of NAPCA will remedy this situation in the near future.

9.2 KRAFT SOURCES

The sampling and analysis of gases and particulates produced during the manufacture of pulp, whether they be in the emission streams or in the atmosphere, has been in a rapidly changing state as the result of continuing application of new technology. The last twenty years has seen progress from the early applications of conventional wet chemical analytical techniques to the development of relatively sophisticated gas chromatographic procedures which permit sulfur-specific separation of a spectrum of sulfur-containing compounds present in the atmosphere and in the pulping process emission streams and final reduction of the analytical data by computer from data logged on magnetic tape. Each of the various available analytical procedures has either served a useful purpose in providing initial identification of the type and magnitude of the pulping industry's air pollution problem or in the immediate and continuous monitoring and control of the unit processes so that the causes of the emissions can be minimized or eliminated.

Major emissions from sources in the kraft process have been identified and characterized in Chapter 4. Particulates of interest include mainly sodium sulfate, sodium carbonate, calcium carbonate, and calcium oxide. The principle gaseous emissions include sulfur dioxide, hydrogen sulfide, and various alkyl mercaptans, sulfides, and disulfides. Many other gaseous compounds are formed in the process or in the atmosphere, but appear in much lower concentration. It must be recognized that suitable methods of analysis are not available for some of the compounds of interest. A review of the available methods for analysis of malodorous sulfur compounds will indicate that many are either inadequate or relatively new and untried. It is apparent that many of the available methods and instruments have not achieved the state of reliability and simplicity needed for routine application.

Control techniques presently available, when applied to kraft sources, may reduce the emission of the hydrogen sulfide to the point where it is no longer the major constituent and may require monitoring of compounds for which we have no satisfactory analytical methods.

9.2.1 SOURCE SAMPLING (GASES)

Analytical techniques have always been an important aspect of engineering development. In 1953, Felicetta, et al. (1) stated:

> "Those interested in kraft pulp production have expended much effort on the development of processes to avoid the discharge of odorous substances from kraft pulp mills. While this effort has resulted in important progress, the problem does not appear to be entirely solved because practical means for complete odor elimination do not seem to have been yet established. A major difficulty in locating odor sources and in testing performance of odor elimination processes has been the lack of accurate and facile analytical methods."

Analytical techniques used in the 50's and early 60's did not produce sufficient data to permit major breakthroughs in odor reduction technology. Wet chemical methods such as proposed by Fellicetta, et al. (1) in 1953, while they did permit determination of the four major malodorous sulfur-containing compounds emitted from the kraft pulping process, were quite tedious and required one man-day to perform two or four analyses. Since two analyses are generally required to establish efficiency of a particular process--up and down stream--little progress could be expected.

Those pioneer chemists who did study process emissions with wet chemical methods or early gas chromatographic techniques reported such wide variations in emission levels from one sample to another that management failed to accept the validity of the data. Within the past two to three years, however, continuous monitoring instrumentation utilized by a number of mills, the National Council for Air and Stream Improvement, and others have produced sufficient data to confirm that processes which were once thought to be at equilibrium are, in fact, subject to frequent and wide excursions in emission rates. Accurate material balances can be attained only by continuous or frequent interval sampling. Variability in composition caused by changes in operating parameters are common in a kraft mill and flow rates vary widely.

9.2.1.1 Odors

Monitoring of odors represents one of the most difficult problems facing workers in the field. Even at source concentrations, methods frequently are not available for chemical analysis of odorous compounds of interest. In several instances the available chemical methods have a sensitivity which is above the human odor threshold for a given compound.

Human sensors suffer from other shortcomings in attempting to "quantify" odor concentrations. Among the factors which influence the individual's response, according to Lindvall (2), are sense of smell, age, hormonal factors, diurnal variation, adaptation, nature and strength of stimulus, motivation, attitude and expectations regarding the experiment, and previous experience. Nevertheless, physiologists feel that these variables can be compensated for and that this is the only method of evaluation available in many instances.

Cederlöf and co-workers (3) designed a single chamber exposure hood and flue gas dilution system which permitted determination of odor thresholds in the field for various flue gases from the kraft process. A number of subjects compared different samples of flue gases diluted with fresh air and decided at what concentration the flue gas odor was no longer noticeable. Estimates of the effects of different deodorizing measures were obtained by taking the flue gas samples from the stack and from various phases of the production process.

Sullivan, et al. (4) designed and installed a six-chamber exposure hood and gas dilution system in a 35-foot bus which could be driven to mill sites to determine flue gas odor detection thresholds and the effects of odor control processes on the detection thresholds of the resultant gases.

Use of human panelists, exposure chambers, and flue gas dilution systems can provide meaningful data which can be directly related to the engineering design and optimem operation of odor control processes.

9.2.1.2 Manual Sampling and Analysis

As indicated in the introduction to this chapter, the proper collection and handling of the sample prior to analysis is as important as the analytical method. Batch samples must be collected and handled with care to prevent sorption and reaction prior to analysis. In some cases, only continuous sampling systems can be used. Particulate matter must be separated from gases insofar as possible in a manner which avoids sorption of the gases or contribution of interferences. The interactions between gases and particulate matter has not been definitely established.

The chemical nature of kraft mill gaseous effluent streams has been studied by a number of investigators utilizing mass spectrometry, gas, and column chromatography. A 1952 mass spectrometric study by Fellicetta, et al. (1) reported that the major sulfur-containing compounds were hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide, whereas sulfur compounds containing ethyl groups were substantially absent. Subsequent investigators have confirmed the identity of the major sulfur-containing gases and have reported lesser concentrations of isopropyl mercaptan (5).

Fellicetta, et al. (1) collected batch samples in evacuated 20-liter bottles. Hydrogen sulfide and mercaptans were determined by potentiometric titration with silver nitrate (6, 7) using a silver wire coated with silver sulfide as the indicating electrode. Aqueous samples are titrated in 1.0 N aqueous sodium hydroxide to which ammonium hydroxide has been added to prevent precipitation of silver oxide. Elemental sulfur interferes with the procedure since it reacts with the mercaptan and the reaction product imparts an electrode potential too close to that of the sulfide ion. The alkyl sulfides and disulfides were then determined by bromate-bromide titration (8, 9).

Although the method did provide limited information concerning the relative quantities of the four major malodorous sulfur compounds present in various process streams, little useful information was thereby obtained describing the relationship between these sulfur gases and process variables because of the tedious and time-consuming nature of the procedure. The usual and understandable response of kraft mill chemists was one of disenchantment with the method because of the unfavorable ratio of useful information to man-hours expended.

Martin (10) utilized a sequential sampler on the recovery furnace stack to obtain a 30-minute sample every two hours over a 24-hour period. One complete cycle of twelve samples was run each weekday. The impinger charge was analyzed for H_2S by argentometric titration.

Wright and associates (11) studied the colorimetric determination of hydrogen sulfide and methyl mercaptan. These authors contended that an analytical improvement was achieved through the substitution of an intermediate color body--Bindschindler's green--for the usual dimethyl-p-phenylenediamine.

In 1957, Colombo, et al. (12) critically evaluated the wet chemical methods then available for the separation and analysis of the major sulfur-containing compound types present in kraft pulp mill gaseous emissions. The Bertgström-Trobeck procedure (13, 14) utilizing selective absorption in solutions of acidified cadmium chloride, mercury cyanide, and mercuric chloride was considered unsatisfactory because of the interference of sulfur dioxide in the determination of hydrogen sulfide. The Wright et al. Bindschindler green method for hydrogen sulfide and methyl mercaptan was considered unsatisfactory because of its low sensitivity and its non-reproducible absorption spectra for methyl mercaptan.

The Fellicetta, et al., method (1) utilizing the $AgNO_3$ stepwise potentiometric titration for hydrogen sulfide was considered inadequate when the ratio of H_2S/CH_3SH is in the range of 10-20/1.

Colombo and co-workers then proposed a selective absorption system in which SO_2 was collected in 0.2 N sodium acetate; hydrogen sulfide in 5% $CdCl_2$-0.2 N HCl; and methyl mercaptan in methanol at -75°C. Analysis was accomplished by oxidizing the SO_2 to sulfate and precipitating and weighing $BaSO_4$; titrating the collected CdS iodometrically and titrating the methyl mercaptan potentiometrically with $AgNO_3$.

The Colombo procedure suffers from the obvious problems of a time-consuming gravimetric determination of SO_2 and the use of a -75°C bath for collection of methyl mercaptan.

Bialkowsky and DeHaas (15) in describing one of the early continuous methods for determining sulfur compounds in mill gases, observed that:

> "the evaluation and control of sulfur losses in sulfate pulping and recovery operations have been limited by the availability of adequate and convenient testing procedures... Thorough investigations by the U. S. Public Health Service (16) have shown that the odor threshold detection values for hydrogen sulfide, methyl mercaptan, and dimethyl sulfide are . . . somewhat less than 1 ppm on a weight basis."

Odor threshold data developed within the past few years have shown these thresholds to be in the ppb or less range.

Bialkowsky and DeHaas cited problems common to wet chemical methods as well as new instrumental methods. For example, they noted that "if oxygen is present, it is often advisable to complete the analyses as rapidly as possible since under wet conditions hydrogen sulfide is oxidized to elemental sulfur and the mercaptans are converted to disulfides."

Bialkowsky and DeHaas also discussed the testing techniques available and in use at that time including precipitation with Hg II (13), potentiometric titration with silver nitrate (6, 7), bromine oxidation in acidified solution using a bromate-bromide solution (8, 9), and the colorimetric determination of H_2S with methylene blue or Bindschindler's green (11). They noted that all of "these procedures are time consuming and often-times the composition of the streams change very rapidly."

Harding, et al., (17) modified the Fellicetta procedure and provided for the additional collection and determination of sulfur dioxide. Sulfur dioxide was determined by the West-Gaeke method. Sulfamic acid was added before color development to eliminate nitrogen dioxide interference. Hydrogen sulfide and mercaptans were absorbed in cadmium chloride and separated by pH adjustment of half the combined precipitate to 1.0 to dissolve cadium mercaptide. The remaining suspension was filtered, the cadmium sulfide precipitate dissolved and the sulfide determined by iodometric titration. The other half of the combined cadmium sulfide-mercaptide precipitate was completely dissolved and titrated iodometrically. The mercaptan concentration was calculated by difference between the first and second titration. Dimethyl sulfide and dimethyl disulfide were absorbed in benzene solution and the RSR-iodine complex measured spectrophotometrically. The remainder was oxidized in standard bromide-bromate for determination of total RSR + RSSR. RSSR was calculated by difference. This procedure also was time consuming.

In 1969, Adams and Wan (18) studied the recovery of hydrogen sulfide in the concentration range of 50-500 ppm by collecting the gas in a Greenburg-Smith impinger containing 100 ml of cadmium chloride solution and titrating the collected sulfide iodometrically according to the NCASI procedure outlined in Technical Bulletin 28 (17). An average recovery of 65 percent was achieved over this concentration range. Simultaneous analysis of the hydrogen sulfide dilutions with a Barton Model 286 showed a relative standard deviation within ±5 percent from the prepared concentrations. The addition of 1 percent STRactan 10 to the cadmium chloride absorption solution improved the recovery to 95 ±5 percent from the prepared concentration.

Batch sampling and manual, wet chemical analysis fail to provide the type of information necessary for effective and efficient process control. The data are not readily available for several hours after the sample is obtained. Even if one could automate the analytical processes by use of a multi-channel Technicon AutoAnalyzer ^{R}, data would not become available for approximately 15 - 30 minutes. Any system which employs one or more steps involving batch sampling and manual analysis techniques cannot be recommended for present day mill process control because of (a) the unfavorable ratio of detail of data obtained to the man hours required to obtain the data and (b) the time lag in obtaining analytical data which lowers its significance to mill operators and management.

9.2.1.3 Instrumental Sampling and Analysis

The problems of representative sampling as described previously are still applicable and must be considered when instrumental sampling is involved.

The dual problem of particulate and water removal from process streams prior to gas analysis must be specifically considered for each analytical method. These problems become more acute as the sampling time and rate increases and generally are most critical for continuous process monitoring.

Blosser and Cooper (29) designed a plastic and stainless steel system which accomplishes the three functions of particulate removal, dewatering, and SO_2 stripping. The primary difficulty in the mill application of this device appears to be in the abbreviated useful lifetime of the particulate filter.

Thoen (58) has applied for a patent on a ceramic and stainless steel probe which is claimed to filter and dewater satisfactorily for longer periods of continuous use.

Probably the most critical part of a continuous process gas monitoring system involves particulate removal and dewatering. Analyzers such as the Barton operate continuously for weeks in the laboratory almost without attention without calibration changes.

However, when automatic analysis instruments are taken to the mill and used as continuous process monitors subtle and/or drastic changes in calibration may take place at anytime from a few hours to several weeks. These changes are generally related to particulate build-up in the sampling line between the source and the detector, excess liquid accumulation in the detector itself, or changes in the air sampling rate.

Careful design of the sample handling system and frequent checking of the effectiveness of the system are required in the early stages of the development of a continuous monitoring program to assure adequate filtration and dewatering. Otherwise, the program may fail.

At the present time, it appears that no completely reliable system has been developed for removal of water and particulates on a continuous basis. Components of a suitable system might include a ceramic or stainless steel filter; a cyclic blow-back to clear the probe of collected particulates; a condenser with drop-leg; and a short, small diameter heated sample line.

A discussion of the separation of particulates from gases would be incomplete without mention of the probability that reactive gases such as hydrogen sulfide, sulfur dioxide, mercaptans, et cetera, will be adsorbed onto the particulates collected by the filter whether it be glassware, ceramic, or a stainless steel frit. Adsorption (possibly reaction) will result in an initial (or sustained) lower apparent sulfur gas concentration. Once an equilibrium has been established between the adsorbing surface and the gas, the apparent concentration will approach the actual concentration. Changes in gas concentration, either up or down, will obviously affect the equilibrium and result in an error in measured or apparent concentration which will lag the actual concentration. The magnitude of these errors can be mathematically modeled for any assumed magnitude of range of gas concentration and demonstrated with an analog computer.

A. pH

Since one practical solution of kraft odor control may well be oxidation of the malodorous compounds to sulfur dioxide (for maximum economical heat recovery as well as odor reduction) and because of the rapidly varying character of the source emissions, Bialkowsky and DeHaas (15) observed that "it is much more important that facile and rapid methods are available for the determination of the total amount of sulfur compounds and sulfur dioxide." Unfortunately, this observation is still true thirty years later.

To this end they proposed the catalytic oxidation of the reduced sulfur compounds to sulfur dioxide and continuous read-out of the resultant variation in pH of a sulfuric acid-hydroxide peroxide collection solution. Total reduced sulfur was determined as the difference between the concentrations of sulfur dioxide in the oxidized and unoxidized emission gases.

Their data first revealed wide, short term fluctuations in emissions of total reduced sulfur compounds not only from the digestors, but the lime kiln and recovery furnace as well. Until this time, the rapid and wide fluctuations in sulfur gas content of the recovery furnace gases had not been recognized. Unfortunately, this phenomenon received little attention by other investigators and mill management during the following fifteen years.

B. Lead Acetate Tape

Mathews and co-workers (20) redesigned the Rubicon acetate tape H_2S instrument for the reliable, continuous duty monitoring of H_2S losses. These instruments were used extensively in their Ohio and West Virginia mills to measure H_2S losses.

C. Ultraviolet

In 1965, Murray and Risk (21) described an ultra violet, real-time hydrogen sulfide analyzer to assess the effects of operating variables on hydrogen sulfide release from a kraft recovery furnace. Sulfur dioxide has strong absorption bands both in the ultraviolet and infrared; whereas, hydrogen sulfide absorption in those wavelengths is unfortunately low. Ultraviolet absorption was chosen for the measurement because stable, moisture-resistant optics could be used. Since sulfur dioxide is present in the recovery furnace flue gas, a double beam instrument was required. Flue gas was split into two streams, one passing through an oxidation furnace where the hydrogen sulfide was converted to sulfur dioxide in the same manner used by Bialkowsky and DeHaas in 1952 and thence to the second optical cell. The difference in the sulfur dioxide content of the oxidized and reference streams was measured as the difference in radiation intensity of the two beams. The primary advantage of this ultraviolet analyzer over the earlier Bialkowsky and DeHaas SO_2 analyzer is related to the substitution of ultraviolet spectroscopy for a wet chemical technique, thereby improving the probability for lower instrument maintenance.

D. Coulometry

Coulometry is based upon the electrolytic generation of bromine from a bromine-containing electrolyte in the absorption-reaction cell. The cell voltage is determined by the concentration of bromine in the electrolyte. The current flow through the bromine generating circuit is controlled by the voltage sensing circuit to maintain a constant predetermined concentration of bromine. As the sample gas containing reduced sulfur compounds (and other bromine-reacting compounds) is drawn through the cell at a constant rate the bromine in the electrolyte is consumed. The resultant drop in bromine concentration is sensed as a drop in cell voltage and the bromine generating circuit is activated to restore the original cell voltage. The additional current flow through the bromine generation circuit is proportional to the quantity of bromine-titratable gases reacting in the titration cell. The generating current readout and the sample flow rate are

are then converted to concentration. Each class of sulfur-containing gases is oxidized by a different quantity of bromine according to the following equations:

$$SO_2 + 6H_2O + 4Br_2 \rightarrow 2H_2SO_4 + 8HBr$$

$$H_2S + 2H_2O + 2Br_2 \rightarrow H_2SO_4 + 4HBr$$

$$RSH + 3H_2O + 3Br_2 \rightarrow RSO_3H + 6HBr$$

$$RSR + H_2O + Br_2 \rightarrow RSOR + 2HBr$$

The Titrilog (22, 23), utilizing this principle, has been successfully used by Troebeck, et al., (24) to provide a real-time evaluation of total reduced sulfur emissions from the small Pena Pobre kraft mill near Mexico City for over twelve years. The Titrilog has provided continuous information describing relationships between changes in process variables and reduced sulfur gas emissions. Significant reductions in emission rates of malodorous sulfur gases from various unit operations with the Pena Pobre kraft mill during this period were achieved and documented. (Parenthetically, it should be noted despite the documented improvement at Pena Pobre, the mill has not achieved an "odorless" operation and that its earlier and present stage of odor emission cannot be directly related to U. S. kraft mill technology since the comparison is between the 40 - 80 tons per day pulp production capacity of Pena Pobre and the 200 - 1200 tons per day pulp production rate of typical U. S. kraft mills.) The new version of the Titrilog reportedly has a sensitivity for H_2S of 0.01 ppm, for SO_2, 0.02 ppm, and for RSH, 0.02 ppm.

The Barton Model 286 electrolytic titrator (25) has been used by a number of investigators for monitoring (26) and control (27) of the emission from kraft mill sources.

Two sampling procedures have been used by Thoen and co-workers. Batch sampling is accomplished by drawing the source gas into a 12-liter evacuated flask through the sampling line containing a glass wool plug at the flask neck. The sample is pumped out of the flask and into the titration cell at the rate of 200 - 300 ml/min. Total sulfur is calculated from the direct analysis of the collected sample. Sulfur dioxide is then removed from the sample gas by absorption in 3 percent potassium biphthalate. The difference in generating current corresponds to the concentration of SO_2 in the grab sample. Other compounds are then successively removed with additional wet scrubbers until only the "residual" sulfur compounds are passed into the titration cell.

Thoen, et al. (27) provide a typical calculation procedure for the analysis of flue gases from a furnace burning oxidized liquor. Several "proportionality factors" were used in their calculations, "most of which were taken from the Barton operating manual."

A word of caution is required at this point. Wan and Adams (28) have compared four Barton titration cells against standard H_2S atmospheres and have found that only one of the cells approximated the manufacturer's reactions factors sufficiently close to be used for quantitative analysis. Each cell should be calibrated against known concentrations and the manufacturer's factors confirmed or new factors calculated. It should also be noted that much of the data in the instruction manual refers to the analysis of natural gas rather than air or combustion gases. The calibration curves provided in the manual are based upon a gas density of approximately 0.65 rather than 1.0.

The Barton Model 286 and the modified Model 400 (25) have been evaluated by NCASI personnel under a wide variety of kraft mill conditions. A detailed description of suitable procedures for using the Barton titrators, including the operation, modifications, calibration, batch sampling and continuous monitoring, has been prepared by Blosser and Cooper (29).

The quantification of each component in a mixture of sulfur-containing gases is not possible without prior knowledge of the ratio of compounds present or through use of a pre-separation procedure. An approximation of the "total" sulfur gases present can be obtained by assuming (or knowing) which of the various possible sulfur gases predominates. There currently is no satisfactory technique other than chromatography for the measurement of SO_2 in a wet gas stream according to Blosser and Cooper.

Thoen, et al., (27) reported the use of a series of wet gas scrubbers to separate sulfur compounds prior to titration. The following scrubbers were recommended:

1. SO_2 removal	3 % potassium biphthalate
2. SO_2 + H_2S removal	1% cadmium sulfate and 2% boric acid
3. SO_2 + H_2S + RSH removal	10% sodium hydroxide
4. SO_2 + H_2S + RSH + RSR removal	0.5% silver nitrate

These authors state that "residual" compounds are not removed by any of these scrubbing solutions. However, no evidence was presented to substantiate this statement.

It should be noted that others (30) have found that the analyzer has severe limitations in the analysis of kraft mill streams that contain all major sulfur compounds in appreciable concentration. Only in measuring emissions from the recovery furnace and lime kiln, which contain low concentrations of organic compounds and high concentrations of inorganic sulfur, has the application of the instrument been satisfactory. In other kraft sources such as washer vents, digester and evaporator noncondensibles, et cetera, difficulty has been experienced in obtaining quantitative separation of the classes of sulfur compounds with the scrubber solutions. The higher concentrations of the organic sulfur as well as high concentrations of alcohols, ketones, and terpenes prevent a good separation.

The unit has as much as a five-minute time constant in the electronics and a five-minute time lapse in the sample system. However, significant fluctuations are recorded as it responds to a concentration increase more rapidly. Absolute values could be in error for rapidly fluctuating concentrations.

Continuous Barton records of TRS from kraft recovery furnaces have shown changes of 200-500 ppm over a period of less than five minutes. If one considers the possible lag effects of (a) gas adsorption on filtered particulates (b) the sometimes-used practice of inserting a surge chamber between the source and the Barton, and (c) response-time of the Barton cell, then it can only be concluded that the observed rapid fluctuations in TRS emissions are in fact more rapid than revealed by the continuous records.

The sensitivity of the newer model 400 is reported (25) to be 0.02 ppm for H_2S, 0.02 ppm for RSH, 0.05 ppm for organic sulfides, and 0.05 ppm for SO_2.

E. Gas Chromatography

The advent of gas chromatography provided the technological means for significant improvement in the number of source samples which could be analyzed per man day and at the same time provided greater detail as to the range of mercaptans and alkyl sulfides and disulfides concomitantly present in the various kraft mill process streams. The gas chromatography provided an inexpensive, alternative instrument to the mass spectrometer for identification and quantification of the many compounds present in kraft mill emissions streams.

Batch Technique. Adams, et al., (31, 32) and Cave (33) reported the earliest applications of gas chromatography to the analysis of kraft process gases. Adams, et al., concentrated the process gases on silica gel in 1/4" x 8" stainless steel tubes at -78°C. After the sample was collected, the tubes were sealed with Swagelok caps. The adsorbed gases were flash desorbed directly onto a 30 percent Triton X-305 column followed by a thermal conductivity detector. Water vapor tended to interfere with the determination of dimethyl disulfide, the latter peak being superimposed upon a broad water peak. Analysis of a single sample for the five major sulfur gases could be completed within thirty minutes.

Adams, et al., (34) conducted an in-plant survey of process emissions at nine West Coast kraft mills utilizing the above technique. Rather widely varying emission rates were found. Several significant observations were reported such as the addition of four gases to the air feed of a black liquor oxidation tower resulted in formation of dimethyl disulfide which was then lost to the atmosphere.

Grune (35) confirmed the GLC separation of volatile sulfur gases in process streams using Triton-coated packed columns and thermister and hot wire thermal conductivity detectors. In addition, he showed that a Triton-coated capillary column provided separation of volatile sulfur gases, although a tailing of the resultant elution peaks was observed

Cave (33) absorbed the emission gases in ethyl benzene at -78°C. The sample was then concentrated by either one or two fractional distillations and the distillate analyzed by thermal conductivity gas chromatography on a TCP column. Approximately two days were required to complete three distillations and analyses.

The subsequent availability of the flame ionization detector (FID) (36) permitted direct analysis of organic sulfur-containing gases without the interference of water. Unfortunately, the FID is also insensitive to H_2S and SO_2. Thomas (5) studied the emissions from five sources at a Maine kraft mill.

Anderson (37) and Ruus (38) studied volatile organic sulfur compounds in the kraft emissions by GLC using a 30 percent Triton X-305 column and FID.

Bethge and Ehrenberg (39) examined the volatile constituents of the kraft pulp mill blow and relief gases by gas chromatography and confirmed the identification of the compounds by mass spectrometry. A number of terpenes and twenty-five other compounds, including hydrogen sulfide, the organic sulfides, and thiophene were identified.

Rhoade (40) described a gas chromatographic system using a thermal conductivity detector for the analysis of recovery furnace combustion products, including carbon dioxide hydrogen, oxygen, nitrogen, methane, and carbon monoxide. He was unable, with the instrumentation used, to determine any of the sulfur gases including sulfur dioxide, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide.

Microcoulometric (MCT) detectors using electrolytically generated iodine (41, 42) and bromine (43) permit determination of all five major types of sulfur-containing gases.

Adams and Koppe (44) used a bromine microcoulometric detector in conjunction with GLC for the direct analysis of sulfur gas emissions from a kraft mill. The MCT detectors also respond to unsaturated hydrocarbons, but the stoichiometry is incomplete.

Brink and co-workers (45) studied the pyrolysis products of kraft black liquor burned in an experimental laboratory furnace. Two analytical methods were used. Gas-solid chromatography (GSC) with a thermal conductivity detector (TC) was used to detect the presence of several gaseous inorganic products. GLC and FID were used to detect the organic gases present. In addition, iodine MCT was employed to complement FID in the quantitative determination of volatile, sulfur-containing pyrolysis products. Brink, et al., converted the various sulfur gases to H_2S by reduction in the presence of hydrogen as they eluted from the GLC column. This provided for maximum detector response as well as yielding a common titration factor for all sulfur compounds present in the pyrolysis mixtures. They selected the reducing mode because it has been shown (46) that conversion of the sulfur in organic compounds to sulfur dioxide is incomplete.

The flame photometric detector (FPD) was developed by Brody and Cheney (47). The flame emission from sulfur-containing compounds is viewed at 394 mμ by a photomultiplier tube.

Alley and Turner (49) described the use of an FPD for the detection of H_2S, CH_3SH, CH_3SCH_3, CH_3SSCH_3 and SO_2 following gas chromatographic separation on a ten-foot column of Triton X-305 on acid washed DMES Chromosorb G. The data show peak height linear with concentration on a log-log plot up to about 150 ppm. A 0.25 ml sample loop was used.

Stevens and associated (50, 51) using an improved model of the FPD, found a linear response to SO_2 over the range of 10 - 700 ppb. In addition, they reported linearity of response for H_2S, CH_3SH and CS_2 in the range of 10 ppb to 10 ppm. Although Stevens' initial application of the FPD was to the direct and gas chromatographic analysis of ppb concentrations of SO_2 in urban atmospheres, there appears to be little doubt that the FPD will be equally useful for the direct GLC analysis of ppm concentrations of sulfur gases in kraft process emissions. The FPD appears to have the greatest range of linear response of any of the presently available GC detectors. Coupled with log electronics, a single sample containing components within a many-fold concentration range should yield to analysis.

Stevens and co-workers (52) have assembled a dilution system to act as an interface between sources of kraft mill gaseous emissions and an elaborate gas chromatographic system using three multiple columns and three detectors. By selection of the appropriate emission gas dilution, they hope to provide detailed chromatographic analyses of (a) the light sulfur-containing gases including H_2S, CH_3SH and SO_2 by FPD, (b) any heavier homologous mercaptans, the alkyl sulfides and alkyl disulfides by FPD and (c) the hydrocarbons by FID. A parallel analysis for "total reduced sulfur gases" will be conducted with a Barton titrator. As late as December 1969, this unit had not been tested in the field.

The data which should be obtained by use of this expensive and complicated analysis system will be extremely interesting from an academic viewpoint. However, because of the expensive and complex nature of the system, it is not planned to have two separate sets of instrumentation to obtain simultaneous data obtained up and downstream from available or experimental odor reduction equipment. Up and downstream data, if obtained, will not be directly comparable because different points in time will be represented.

(In this regard it should be noted that continuous, simultaneous analyses of process gases with two Barton analyzers have revealed rapid fluctuations in both up and downstream emission concentrations in several kraft mills. Such fluctuations will not be as readily observed with a batch gas chromatographic technique involving three chromatographs sampling one source at a time.)

Walther and Amberg (53) assembled a mobile gas chromatographic laboratory for source gas analysis at their widely separated company mills. The sample system includes a ceramic type probe for installation in the process line, a heated sample line, a heated sample conditioner which houses the rotameter and pressure control valves, and a vacuum pump. The sample system draws a sample from the process stream by means of the pump, filters it twice and delivers it to the analyzer at constant temperature and pressure. Part of the sample flow is split at the sample conditioner to by-pass the chromatograph, thereby reducing the lag time to the chromatograph to about 20 seconds. The sampling line is 1/4 inch stainless steel tubing, electrically traced, insulated, and enclosed in a vinyl jacket. Three sampling lines totaling 250 feet are carried in the van. The chromatograph system consisted of five modules: (a) analyzer system, (b) controller section, (c) programmer module, (d) readout system, and (e) sample system. Both thermal conductivity and flame ionization detectors were used with three columns and two column ovens. In addition, the mobile lab carries equipment for sampling particulate emission. A Barton Titrator was also available for analyzing the gases from the recovery furnace and lime kiln.

The work of Williams and Murray (54) must be noted here. These authors reported an enhancement of the conversion of methyl mercaptan to dimethyl disulfide in the presence of heated stainless steel.

Process Techniques. Walther and Amberg (55) prepared a set of specifications for a recovery furnace process chromatograph and submitted them to instrument manufacturers for bid. Beckman Instruments responded with an acceptable proposal. The resultant process gas chromatographic unit was installed at the Crown-Simpson kraft pulp mill at Samoa, California. The chromatograph was designed to provide a measurement of hydrogen sulfide, methyl mercaptan, and sulfur dioxide at ten-minute intervals. The process chromatograph uses two columns to permit automatic back-flushing of the heavier flue gas constituents from one column while the three lighter compounds of interest are being separated on the other column. Frequent data points are obtained to guide in the operation of the recovery furnace.

Applebury (56) and Schaer developed a process gas chromatograph utilizing a modified bromine microcoulometric detector. The chromatograph has the capability of converting the output signal from the microcoulometer to a binary signal. This signal passes through a digital translator changing the signal to an ASCII code, which in turn is fed to a teletype. A punched paper tape record is produced which serves as an input to a Hewlett Packard 2116A computer which prints out peak areas.

Wan (57) and Schaer improved the response of this chromatograph by changing the microtitration cell electrolyte formulation, positions of the titration electrodes within the microcell, substituting a GC column packing with lower sulfur gas affinity, replacing all tubing and connections with Teflon or stainless steel. Samples are analyzed within 15 minutes. The instrument performed successfully for ten months without major technical problems.

F. Selective-Ion Electrode

Orion (59) manufactures a number of solid-state electrodes which have high anionic selectivity and sensitivity. Their sulfide electrode is claimed to be free from interference from chloride, fluoride, sulfate, carbonate, hydroxyl, and phosphate ions. Light and Swartz (60) have studied the use of this electrode in a system to monitor sulfide in spent black liquor from the kraft pulping process. Megy (61) evaluated the Orion sulfide electrode for possible continuous determination of sulfide ion activity in kraft process streams and effluents. It was not found applicable, probably due to rapid deposition of organic material on the membrane.

Despite the possible inapplicability of the sulfide electrode for the direct measurement of sulfide in a complex mixture such as spent black liquor, the electrode appears to have a high potential for measuring sulfide in process off-gases. A gas sample could be continuously passed through a counter or concurrent scrubbing system and the absorbing liquid drained through a cell containing the sulfide electrode. Changes in measured voltage from the sulfide electrode are readily calibrated and recorded.

A line of ion-selective measurement systems designed by Foxboro specifically for on-line industrial applications has just been announced (62). Reported capabilities include: fluoride, chloride, sulfide, silver, copper, cyanide, and a divalent cation electrode for measuring water hardness.

Field evaluation under a variety of conditions will be required to establish the reliability and range of application of the sulfide electrode in the kraft pulping process. In the meantime, it is an interesting research tool.

G. Infrared

Thoen and Nicholson (63) utilized a dual 10 meter path infrared instrument in conjunction with gas chromatography to identify approximately twenty compounds in off-gases from the black liquor recovery furnace, multiple effect evaporators, digestors, black liquor recovery furnace, multiple effect evaporators, digestors, black liquor oxidation tower, dissolving vent, and lime kiln. Although infrared identification is not recommended as a primary analytical method for process gases, it did provide excellent confirmatory identification for gas chromatographic peaks. This must be considered a research technique at this time. The experience of these researchers indicated that several compounds could be identified from a single sample with no pre-treatment other than removal of water with anhydrone.

The identification of carbonyl sulfide in recovery furnace gases and its increase in concentration as the furnace atmosphere becomes reducing is considered one of their most important findings.

9.2.2 SOURCE SAMPLING (PARTICULATES)

Isokinetic sampling is frequently considered important in the proper sampling of particulate emissions from kraft mill sources. However, the test procedure specified by the Industrial Gas Cleaning Institute (71) indicates that "most scrubbers are such that the larger particles are collected with virtually 100 percent efficiency, while a proportion of the particles below 5μ may escape." Although IGCI recommends that isokinetic sampling may be necessary to determine the concentration of dust entering the collector, "a simplified sampling procedure is usually permissable for the determination of the dust concentration in the scrubber exit gases."

It is obvious, therefore, that a rational decision to use or ignore isokinetic sampling procedures must be based upon a prior determination of the particle size distribution of the specific source gas to be sampled. "Once systematic sampling has proved the particulate matter all to be below the size (approximately 5 μ) for which such sampling procedure is necessary, future sampling need not be isokinetic." (69)

If isokinetic sampling is found to be necessary, the Western Precipitation (65), ASME Power Test Code (66), and IGCI (72) procedures provide descriptions of the use of a series of nozzles of varying diameter and a constant sampling rate to provide the desired match between probe and duct gas velocity. However, it is important that the nozzle be not less than 1/4 inch diameter (66).

Duncan and Cooper (74) in NCASI Technical Bulletin No. 41 provide a complete review and instructions for conducting simultaneous velocity and particulate sampling in a duct.

It is also possible to achieve isokinetic sampling with a single nozzle diameter by varying the flow rate of the sample pump. This condition is most readily achieved by use of a null probe and manometer which measures the differential pressure between the interior and exterior of the probe. The operator can then continually readjust the sampling rate to maintain the "null" condition of no pressure differential across the manometer. A commercially available stack sampling kit utilizing this principle is available (77). Unfortunately, errors have been reported of lack of reliability of the null system in low velocity (1000 ft/min) gas streams (69).

In 1947, Collins (64) described a sampling and analytical procedure for measuring the sodium and sulfate loss from a recovery furnace. Since then several detailed and authoritative descriptions of acceptable methodology have been published (65 - 75). At this writing there is no one universally accepted technique for determining particulate emissions from such sources as the kraft recovery furnaces, lime kilns, or smelt tanks. The Industrial Gas Cleaning Institute (IGCI), founded in 1960, has developed detailed methods which are most frequently used by equipment manufacturers when establishing the performance guarantee characteristics of industrial gas-cleaning equipment. These IGCI methods have been prepared and agreed upon by more than twenty-five of the leading manufacturers of industrial gas-cleaning equipment.

Several recommended methods exist for collecting samples of particulate matter from kraft mill emissions; i.e., the 1969 Oregon and Washington "Basic Considerations Re Monitoring Programs for Kraft Mills" which utilizes a modified NCASI sampling train consisting of a 1-gallon knockout bottle, Greenberg Smith impingers, and a glass fiber filter in series. The IGCI manuals (71 - 73) present vital details for properly measuring gas velocity, temperature, water content and selecting pilot tubes and traverse patterns. A filter or other collector is specified which demonstrates 99+ percent collection efficiency for particles of the approximate size analysis to be encountered during the test.

The batch sampling of solids emissions has the same inherent limitations in process control as in the case of gaseous sampling techniques, since the data do not become available until it is too late to take corrective action. Rapidly varying loss rates associated with "normal" operating procedure as well as with process upsets have remained unrevealed until recently when continuous analysis techniques have been utilized. As a result, both large and small differences between a series of batch samples have frequently been attributed to sampling and analysis errors rather than real process operating variables.

Leonard (78) described a continuous particulate analyzer for monitoring soda losses from the recovery furnace electrostatic precipitators. He assumed a linear function between the conductivity of the aqueous collecting media and the collected sodium sulfate. The continuous particulate recorder trace revealed wide and rapid fluctuations in particulate emission which could be related to furnace operating conditions. Having established the authenticity of a wide range of particulate loadings over a short time span and the relationship between the higher emission rates and process parameters, it was possible to correct conditions associated with maximum emission rates.

Camacho (79) described the use of a glass electrode sensitive to sodium ions (and other monovalent positive ions) for monitoring kraft mill stream soda losses. It was concluded that the sodium electrode was as accurate as the flame spectrophotometer for total sodium ion determination under conditions existing in the kraft mill streams. Although the sodium ion electrode was used as a spot check tool, its potential for conversion to a continuous monitoring system is obvious.

Cooper and Haskell (80) used a light scattering bolometer to measure continuously particulate concentration in a kraft recovery stack.

Comparison of the problems associated with wet methods for particulate measurement using the conductivity and ion-selective electrode concepts with the bolometric method results in a trade-off of maintenance problems and the dynamic range of particulate loadings which can be measured and recorded. Sampling probes used for removing solids from the stack should be operated isokinetically, the probe can become plugged, the liquid media can vary in flow rate or cease flowing, et cetera. The light source and detector in optical devices, such as the bolometer, must be frequently cleaned, the light and/or photosensing device can change in intensity or sensitivity with time, and optical devices are non-specific for sodium sulfate. Because of the non-specificity of the bolometer, it will provide assistance in a general mill program to minimize solid losses from the recovery furnace, but it will not provide a direct measure of specific chemical losses.

Achinger and Shigehara (81) have developed a "guide for selecting sampling methods for different source conditions." These authors classified all possible combinations of time and cross sectional variations of the ductwork into four categories. Sampling approaches were suggested for each category which are dependent upon the source conditions existing at the time of sampling. These procedures permit collection of representative data with a minimum of work by the sampling team.

9.2.3 SOURCE SAMPLING (NON-SULFUR COMPOUNDS)

Non-sulfur-containing compounds in recovery furnace combustion products were examined by Hendrickson, et al. (82). Ten kilograms of saltcake dust obtained from an electrostatic precipitator were benzene-extracted and separated on an activated alumina column. Polynuclear aromatic hydrocarbons including benzo[a]pyrene, benzo[e]pyrene, benzo[g, h, i]perylene, chrysene, coronene, fluoranthene, and pyrene were identified by their ultraviolet absorption spectra. Tentatively identified were anthanthrene, anthracene, phenanthrene, and vanillan.

9.2.4 RECOMMENDED SOURCE METHODS

Selection of Applicable Methods for Source Gas Emissions.

Selection of the optimum sampling and analysis technique for specific sources in the kraft mill must be based upon prior knowledge of the approximate composition and concentration ranges present and, most importantly, the proposed use of the data obtained. It is essential to state clearly the objectives of the sampling program and to define the use of the data prior to the selection of the most suitable method. While it may be understood that the recommended methods are to be used for research, no single method can satisfy the requirements of the spectrum of research problems associated with emissions from the kraft mill.

For example, a complex objective might be to provide a complete characterization and inventory of all hydrocarbons and sulfur-containing gases in each malodorous emission source within the mill. A research, dual column gas chromatographic technique utilizing a sulfur-selective detector and a flame ionization detector would be required for this application. The columns best suited for this application include Triton X-305 (28), Dow Corning 710 silicone oil (32), polyphenyl ether (48), and carbowax 20 M (47). This technique will permit differentiation between organic and inorganic, sulfur-containing compounds.

Because of the complex nature of the usual FID chromatogram, a "time-of-flight" type of mass spectrometric analysis of a split stream from the chromatographic column would provide confirmatory identification as well as information describing the many presently concomitantly present and as yet unidentified non-sulfur organic gases. The use of "time-of-flight' mass spectrometric in conjunction with GLC has not been reported in relation to the kraft mill gases. The data thereby obtained will be of greater academic than practical value. Infrared identification has been used but the method has insufficient sensitivity to detect many of the peaks. In addition, considerable time would be required to provide a complete analysis.

A less complex research goal would be a mill-by-mill quantitative inventory of the five major sulfur-containing gases designed to reveal a range of emission concentrations from various processes within each mill and between mills. A sulfur-sensitive detector, either flame photometric or microcoulometric, should be used in conjunction with gas chromatographic separation. Attention must be given to the dynamic response range of the detector used. Concentrations ratios among SO_2, H_2S, CH_3SH, RSR, and RSSR in source gas emissions may require the analysis of a small sample volume first to obtain a quantitative measure of the major compounds. A large sample would then be injected, the elution of the major compound(s) vented, and the eluent then switched back through the detector (44). The addition of a FID detector would not complicate such a system and would provide dual analysis of the organic sulfur compounds. Process application of the FPD and MCT have been limited due to narrow "linear" calibration (log-log) of the FPD and maintenance of the MCT detector. The FPD can be used only at low concentrations (less than 10 ppm, possibly). Adjusting sample volumes to meet this requirement might require a different sample volume for each sulfur compound. The value of the MCT and FPD would be to detect the inorganic sulfur and to determine incomplete separation of sulfur components detected by the FID. Research data thus obtained would be of great practical value in relating odor emission rated to process variables, particularly if simultaneous samples were obtained up and downstream from odor control equipment.

Perhaps the most useful research method for kraft mill process odor control, (considering the present state-of-the-art of the operation of the kraft process) would involve continuous, real-time analysis of total reduced sulfur (TRS) gases or the major reduced sulfur gas in the emission source under study. Because many mills have demonstrated wide and sudden fluctuations of sulfur gas emissions, realtime analytical data can be most readily correlated with the numerous process parameters already recorded in the mill plus those which could be additionally measured and/or recorded. For example, additional measurements including flame temperature, liquor drop size, liquor temperature, and percent black liquor oxidation would be useful in the case of the recovery furnace.

Realtime, broad spectrum continuous analyzers are recommended to achieve this objective. Considerable mill experience is available to confirm the usefulness of this approach. The Titrilog, as well as the Barton Model 286 and Model 400, are well suited for this work. The addition of a pre-scrubber to remove SO_2, for example, provides separation of the major non-malodorous volatile sulfur gas from malodorous sulfur-containing gases.

Mill experience with TRS-types of coulometric analyzers has not been entirely satisfactory. Problems have been encountered which limit the reliable, continuous application of these instruments. These major problems include (a) inadequate probe for dust removal, (b) inability to maintain a constant air flow rate through the coulometric cell, (c) electronic malfunctions, and (d) unsatisfactory state of liquid pre-filters for separating the various sulfur-containing gases in the kraft process emission gases.

At the risk of repetition it is implicit that the essential objective of source sampling and analysis must be properly identified before methods are selected for use. Presumably, the most important research objective of the kraft pulping industry is to reduce to a minimum the emissions of the primary and already identified particulate and malodorous compounds by correlating total reduced sulfur emissions with process variables and then confining mill operations within a specified range of conditions.

Once the achievable reduction in emissions has been attained by presently known control techniques and proper equipment operation and the effect upon the community response or ambient air quality evaluated, then the more complex and sophisticated techniques of Stevens, et al., (52) can be applied to define any remaining problems. If these complex and sophisticated analytical methods for process evaluation are used prior to attainment of the major reductions in emissions which can now be achieved utilizing known and proven techniques, the acceptance of these control techniques will be delayed because of the greater time and effort required to obtain the detailed inventory and relate the mass of collected data to process parameters versus the relatively simple total reducing sulfur gas method. Furthermore, once the known control techniques have been applied to the process, the remaining gases will still have to be subjected to the complex analytical techniques to indicate the additional control methods required to effect further emission reduction.

Other Analytical Approaches. Less experience has been obtained with the Risk and Murray UV H_2S analyzer (21). The commercial availability of such an instrument is not known. The FPD used in conjunction with preselective filters might well provide a more reliable approach to real time analysis than the Barton coulometric detector because of the obvious maintenance advantages of solid state over wet-chemical detectors. However, other maintenance problems would be introduced such as the flow regulation of combustion gases, but these should be relatively minor. In the absence of extensive field use, the FPD and UV methods cannot yet be given an unqualified recommendation as process monitoring or control devices in their present state of mill experience.

9.2.5 AMBIENT SAMPLING (GASES)

Much of the literature published prior to 1966 (and even some of the more recent publications) related to the determination of hydrogen sulfide, methyl mercaptan and the alkyl sulfides and disulfides present conflicting and erroneous conclusions. Publication of new research information since 1966 has provided numerous explanations for these previously observed paradoxes. Thus, in 1969 one must conclude that regardless of the scientific integrity of the investigators who published ambient sulfur gas data prior to 1966-1968, these data may well be in error by as much as one to three orders of magnitude.

The primary sources of these errors may be classified as (a) inaccurate knowledge of the odor thresholds for the malodorous, sulfur gases, (b) acceptance of the published calibration curve for the lead acetate tape method, and (c) the unrecognized significance of the photodecomposition of collected cadmium sulfide in the ppb concentration range which resulted in losses up to at least 80 percent prior to colorimetric determination of the collected sulfide by the methylene blue procedure.

Even as late as January 1968, explanations for anomolous field measurements of hydrogen sulfide were partially attributed to published hydrogen sulfide odor detection threshold concentrations which were in error by 10-500 fold (83). Recently published works indicate that the odor threshold for hydrogen sulfide may be in the range of 0.4 to 4 ppb (84-87, 2), whereas it was previously thought to be in the range of 30-100 ppb (88, 89). The improvement in definition of odor thresholds resulted from the development of reliable, dynamic techniques for the production of sub-parts per billion concentrations of gases, critical examination of the errors associated with pre-1966 analytical methods, and the development of new analytical techniques and instrumentation.

The lead acetate tape had been considered as a reference procedure for the determination of the two-hour average concentration of hydrogen sulfide in numerous field studies conducted spots exposed to light and laboratory air faded seriously. They further reported that lead sulfide exposed to ozone and sulfur dioxide faded significantly in even less time. They concluded that the fading of the lead sulfide spots during sampling and the interval between sampling and analysis reduced the status of the method to a "qualitative indicator of the presence of hydrogen sulfide, but that a negative test was not conclusive." The confusion which resulted from "negative" lead sulfide tape samples was highlighted in a 1963 study in the vicinity of a kraft pulp mill in which the odor of hydrogen sulfide was clearly identified while at the same time negligible response was obtained with the tape samplers (91).

Using reliable gas dilution techniques it has recently been shown that the lead acetate tape is not discolored at 35 ppb H_2S (92) produced from permeation tubes (93) and that the threshold concentration of approximately 50-60 ppb H_2S is required for production of a lead sulfide color on impregnated cellulose tape (94).

These data provide a sound explanation for much of the paradoxical data provided by the lead acetate tape technique since 1954.

The difficulty in providing rational explanations for the ability of trained personnel to detect the odor of hydrogen sulfide while conducting field sampling was frequently compounded by the general agreement which was found between the lead acetate tape method and the widely used cadmium hydroxide slurry-methylene blue method described in 1957 by Jacobs, et al., (95). Since these two diverse sampling and analytical methods usually provided comparable concentration data, it was logical to conclude that both methods were reliable.

When these methods were applied to the calibration of gas dilution systems designed to produce H_2S concentrations in the 0.3-30 ppb range, it became obvious that either the sampling and analytical methods were inadequate or that a serious engineering error had been made in the design of the gas dilution equipment (96). At this same time Sanderson, et al., (90) verbally presented their information describing the shortcomings of the lead acetate tape procedure at the 1965 Air Pollution Control Association meeting in Toronto. Adams and co-workers then examined the Jacobs wet chemical method and found that the precipitate cadmium sulfide was photodecomposed and that the addition of 1% STRactan 10 (97) minimized this decomposition thereby providing reproducible data (98). The reliability of the STRactan modification has now been confirmed in the field by the Bay Area Air Pollution Control District (99).

The foregoing background discussion will provide a perspective for the more detailed discussion of the many atmospheric methods which have been proposed and used to varying degrees for the determination of ppb atmospheric concentrations of the malodorous, sulfur-containing gases found in the vicinity of the kraft pulping process.

9.2.5.1 Odors

No present instrument or chemical analysis can fully replace the human nose. Unfortunately this sense is extremely subjective and quite variable in its response. In some instances, such as malodorous emissions from kraft pulp mills, members of the lay public will claim to identify the malodor. However it is commonplace for several persons detecting the odor at the same place and time to describe it differently(100). The quality of an odor will frequently change with dilution as the observer progresses away from a source. This change may be due in part to a difference in response to the concentration gradient of a given malodor or it may be due to the varying detection thresholds of a number of different malodors present in a complex mixture as exemplified by the kraft mill emissions. The problems described in Section 9.2.1.1 apply equally as well here.

A. Community Odor Panels

In situations where a single source apparently is responsible for odor complaints a continuing community odor survey may be a valuable technique to evaluate the effectiveness of odor abatement methods. To be of value, the survey must be conducted on a daily basis over a period of years to establish trends. The results of an occasional survey will have no significance because of day-to-day, ground level variations within the normal odor intensity range for a given level of odor emission related to the influence of meteorological variables.

The value of an organized, continuing community odor survey is exemplified by the many years of observations by an odor panel living in the vicinity of the Peña Pobre kraft mill near Mexico City (101). The mill utilizes the services of a large number of volunteer observers distributed throughout the area of historic odor complaints. These observers are unpaid and were primarily selected from the group of original complainants. The observers are furnished a weekly report card, providing spaces for recording the time of day, the day of the week, the observed strength of the odor, and the quality of the odor. These cards are then returned to the mill. All weekly records are composited and related to the sequencing of blow operations. The weekly correlations are further reduced to a yearly trend value relating the number of complaints or observations of odor divided by the number of observers reporting divided by the number of blows per day. This evaluation program has been in continuous operation since 1957 prior to the installation of odor control processes. These empirical values expressing community odor have gone from 0.7 in 1957 to less than 0.01 in 1962. This record provides management with an objective evaluation of the effectiveness and value of their odor control installations.

This simple technique provides evidence, albeit subjective of the effectiveness of odor control techniques as measured by the observers' responses.

Odor surveys have been conducted in other pulp mill communities, but with much different objectives. A community survey in the vicinity of Lewiston, Idaho, (102, 103) was designed to determine the nature and extent of air pollution in the area and to attempt an analysis of the "environmental stress of air pollution" on a population sample. High school science students recorded their subjective response to odors detected three times daily, morning, afternoon and evening. Since the study was of short duration and no major mill process changes were involved, the study merely indicated that odors were present and that the students identified additional community odor sources including burning garbage, cattle odors, and commercial food processing odors.

Cederlöf, et al., (85) determined the odor threshold for kraft mill flue gases to provide a basis for calcuations of the dilution with air required to ensure freedom from odor. Thirty-six subjects were tested according to the principle of paired comparisons between test gases and fresh air. The technique revealed that black liquor oxidation and a "chlorine scrubber" reduced the odor threshold of recovery flue gas by approximately one power of 10 and by two powers of 10, respectively. These data showed a correlation between the concentration of sulfur compounds present in the test gases and the observed odor thresholds.

Sableski (104) outlined a guide to the selection of observers, evaluating sensitivity and making odor measurements either on a subjective intensity scale or with Scentometers to estimate odor intensities.

B. Scentometer.

Huey, and co-workers (105) developed an inexpensive, portable device known as the Scentometer which has been used to contribute greater quantitative significance to the subjective evaluation of odor concentration by field observers. Prior to this development in 1960, observers rated odors on some arbitrary numerical scale (for example, 0-5) which subjectively described their response from "undetectable" to "overpowering." With the Scentometer an observer can provide an order of concentration magnitude of the malodorous gas in terms of the number of volumes of clean air required to dilute the malodor to its detection threshold. Four dilution levels are available 2, 8, 32, and 128. The low number of dilutions are sufficient in field application to provide rapid, inexpensive and meaningful data in terms of the degree of odor reduction which would be achieved by a given reduction of malodorous emission from a known source. It is recognized in the use of this device that variations among individual observers and the variability of an individual with time is of sufficient magnitude that the limited dilutions provided by the Scentometer are inadequate for field evaluations of concentration. Any semi-quantitative use of this device would be predicated upon knowledge and application of known principles of sensory fatigue, individual variations in odor threshold, and the effects of recent eating, smoking, physical condition, etc.

9.2.5.2 Hydrogen Sulfide

A. Lead Acetate Tile

Chanin, et al., (106), suggested that ceramic tiles soaked in an aqueous solution of lead acetate, acetic acid, and glycerol, when exposed to outdoor air containing hydrogen sulfide, could provide a semi-quantitative measure of hydrogen sulfide level by visual estimate of the darkening of the tile. Tiles were examined twice daily and the cumulative darkening recorded. One of the problems encountered was the fading of the lead sulfide color.

Gilardi and Manganelli (107) provided a comprehensive evaluation of the influence of exposure variables upon the developed lead sulfide color. They concluded that the tile had an upper useful exposure limit of 8 hours and that the tile had to be exposed in a light-proof chamber designed to minimize air movement. The surface darkening was measured with a reflectance attachment to a Spectronic 20 colorimeter. They developed a quantitative expression of exposure units:

$$\frac{\text{mg. x hrs.}}{M^3}$$

in which there was a direct relationship between the exposure concentration in mg/m^3 and the hours of exposure within the limits stated. It is not known whether laboratory evaluation of the tiles and development of the above mathematical relationship was based upon reliable H_2S concentration data. It may be that the lead acetate tile has a response threshold similar to that shown by the lead acetate tape and thus would not correlate well at H_2S concentrations in the vicinity of the threshold concentration for human sensory detection.

B. Paint Darkening

Qualitative evaluation of atmospheric hydrogen sulfide has been made by measuring the darkening of test panels coated with lead-base paint (108). Following 30-day field exposures, the amount of paint darkening was reported as a percentage decrease in light reflectance. A method to keep the paint surface wet must be developed if paint darkening measurements are to be at all useful because of the significant influence of humidity upon the rate of color development.

Filamentous growths of bacteria may develop on painted surfaces during periods of high humidity and be confused by the layman for hydrogen sulfide-induced paint darkening. Mildew may be readily identified under low power magnification or its removal by five percent sodium hypochlorite solution.

Wohlers and Feldstein reported that the incidence of lead-base paint darkening is time-concentration dependent following the equation:

$$C = \frac{0.099}{t} + 0.001$$

where

C = H_2S concentration, ppm vol.

t = time, hours

Surfaces freshly painted with lead base paints appear to be resistant until weathered for approximately ten months.

Despite the myriad variables controlling the onset of paint darkening, H_2S concentrations above 50 ppb for several hours under optimum conditions will darken paint. This reported paint darkening threshold appears to agree with the similar threshold reported for the lead acetate tape.

Reffner, et al., (109) studied the H_2S discoloration of exterior paints containing heavy metal salts as pigments or fungicides. An electron microscope technique was developed which identified lead sulfide and mercuric sulfide on the surface of discolored paint.

C. Metal Tarnishing

Wohlers and Feldstein (108) found that H_2S concentrations above 3 ppb for more than 40 hours will tarnish sensitive metals such as silver and copper. Insufficient reliable quantitative experience has been obtained to develop meaningful relationships between average H_2S exposure concentrations and tarnishing. Although the National Air Sampling Network "Effects Package" utilizes silver plated panels, no H_2S concentration information is available to develop a meaningful correlation between reflectance loss and intensity of H_2S exposure.

Falgout and Harding (83) described a dynamic sampling method for the determination of hydrogen sulfide and methyl mercaptan by measuring the decrease in reflectance of silver membrane filters through which air had been drawn at a known rate for a selected time period. The method depends upon the reaction between metallic silver and hydrogen sulfide.

These authors suggested that their inability in 1965 to determine hydrogen sulfide in the air of Jacksonville, Florida, by the methylene blue method when the odor of hydrogen sulfide was detected might be due to the presence of interfering substances such as ozone. Based upon present knowledge (98) it seems more reasonable to postulate that the collected cadmium sulfide photodecomposed prior to the determination of the sulfide by the methylene blue colorimetric procedure.

Falgout and Harding studied the possible interference from nitrogen dioxide, ozone, and ultraviolet light upon the silver membrane filter. It was concluded that the silver membrane response to hydrogen sulfide and methyl mercaptan was not affected by other commonly encountered pollutants and that the filters could readily be protected from ultraviolet light and atmospheric particulates by wrapping the filter with black tape and placing a cellulose filter ahead of the silver membrane filter. As applied by the authors, air was sampled at the rate of 0.9 lpm and provided 23-hour average concentrations of sulfide and mercaptan reported as $\Delta R/m^3$.

It appears that further evaluation of the silver membrane technique should be undertaken under controlled conditions in which ΔR is related to known concentrations of H_2S generated by the permeation technique.

D. Chemically-Treated Filter Tape

Sequence samplers using chemically-impregnated tapes have been used widely to determine average ambient air concentrations of selected compounds for designated periods of time--for example, two hours.

In the most popular, commercially available tape samplers, air is drawn through a lead acetate-impregnated tape for a predetermined time, leaving a darkened area when hydrogen sulfide is present in the air. The exposed tape is then returned to the laboratory and optical density determined (110). The optical density of the spot was reported to be proportional to the hydrogen sulfide concentration.

Two-hour average hydrogen sulfide concentrations have been determined in many localities using the AISI sequential tape sampler (111) or similar instruments (112-114). In most field applications there is a variable time lapse between the first sample on a roll of tape and the final sample several days later when the tape is returned to the laboratory and the density of each spot photometrically determined. There is conflicting opinion concerning the stability of the lead sulfide color with storage either on the roll in the tape sampler or subsequently in the laboratory when analysis is delayed or when the tapes are exposed to air or light (90), (103).

Subsequently, improved sequence tape instrumentation became available which provided instantaneous photometric read-out of the developing spots throughout the sampling period (111) or a single, automatic read-out upon completion of the sampling period (114). Short-term fluctuations in H_2S concentration are then calculated from the slope of the recorder tracing. This immediate read-out should minimize possible fading of the lead sulfide spots, since no more than two hours of storage is involved. This approach, however, has an inherent source of error because of the reported instability of the PbS color in both sun and laboratory light (90, 115).

According to the instrument manufacturer's calibration curve, the minimum two-hour average HS concentration detectable by the lead acetate tape method is approximately 1.0 ppb (111). At least two laboratories, however, have been unable to produce lead acetate tape darkening until minimum threshold concentration of 50-60 ppb H_2S has been exceeded irregardless of the exposure time (92, 94) utilizing a well-designed gas dilution panel and a H_2S permeation tube, respectively. Therefore, it is theorized that the original calibration curve was developed by either (a) adding the total quantity of H_2S present in the total volume of air to be sampled in a 2-hour period as a single concentrated slug and then passing air through the tape for 2 hours or (b) inadequate dilution techniques were available for use in 1954.

The 1963 report (91) that lead acetate tape gave negligible response when the odor of hydrogen sulfide was detected was undoubtedly due to the recent observations that the spots fade on storage and under light, that the color formation is modified when sulfur dioxide is present, and lead acetate tape will not discolor until at least 50-60 ppb hydrogen sulfide is present. Although the earlier literature reports that the odor threshold for hydrogen sulfide is in the order of 30-100 ppb, more recent studies utilizing more refined techniques for production and chemical determination of low concentrations indicate that the odor threshold for hydrogen sulfide may be in the order of 0.4 to 4 ppb.

Pare (115) confirmed many of the Sanderson, et al. (90) observations about the inadequacies of the lead acetate tape and suggested the use of a mercuric chloride impregnated tape. The resulting spots were reportedly stable even when exposed to 10 ppm of ozone for three days. Pare's mercuric chloride tape was complicated by the need to develop the color of the spot in the laboratory just prior to photometric measurement. Also, mercuric chloride corrodes the metal parts of presently available tape samplers. Substitution of more resistant metals such as stainless steel might eliminate this problem, but raise the cost of instrumentation.

Hochheiser and Elfers (116) have devised a one-step mercuric-type tape which eliminates the need to develop the mercury sulfide in the laboratory prior to photometric measurement. This improved technique appears promising, but will require additional laboratory and field testing before adoption as a "standard" method.

E. Adsorption Sampling

Buck and Gies (117) proposed collecting atmospheric hydrogen sulfide in dry sorption tubes packed with glass beads treated with $KHSO_4$ and Ag_2SO_4. The collected sulfide was dissolved with a solution of $ZnCl_2$ in concentrated hydrochloric acid and the liberated hydrogen sulfide determined by the molybdenum blue method. The hydrogen sulfide test atmospheres were in the range of 200-300 ppb, well above values normally found in the atmosphere.

Although the authors carefully considered a wide variety of possible interferences from other air pollutants, the validity of their hydrogen sulfide test atmosphere was not adequately established. Air oxidation, light sensitivity, storage delays, etc. which have been shown to affect adversely cadmium sulfide (98) and lead sulfide (90, 115) were not evaluated as possible sources of similar errors when collecting hydrogen sulfide with the silver sulfate sorption tube.

A relative detection limit of 0.009 mg H_2S/m^3 (6.5 ppb)

for a 30 minute-sample and 0.02 mg H_2S/m^3 (14 ppb) over a 15-minute sample cycle was claimed for the Ag_2SO_4 sorption method. Extrapolated to a 2-hour midget impinger cycle, this would be equivalent to a sensitivity of 2.2 ppb H_2S.

Buck and Gies concluded that the above sensitivities were "below the odor threshold (approximately 0.05 mg/m^3)." This conclusion is questionable, since the odor threshold for hydrogen sulfide is actually in the order of 0.4-4 ppb (0.00056-0.0056 mg/m^3).

F. Cadmium Hydroxide-Methylene Blue

Sequence samplers using absorption solutions in manifolded impingers have been used to determine average ambient air concentrations of selected compounds for designated periods of time; for example, two hours.

Because sulfide standards have been observed to decrease rapidly in concentration in dilute alkaline solution, many absorption solutions have been examined in an attempt to minimize this loss and permit the subsequent colormetric analysis of the collected sulfide. An excellent review covering the literature to 1957 has been published by Jacobs, et al. (95). Sulfide stablization techniques have involved the precipitation of metal sulfides with zinc (118) and cadmium (119). Jacobs, et al. reported that a cadmium sulfate-sodium hydroxide absorbant was preferable to zinc acetate or ammoniacal cadmium chloride.

In the Jacobs method, hydrogen sulfide is absorbed in an aqueous, alkaline suspension of cadmium hydroxide prepared by dissolving 4.3 grams of cadmium sulfate ($3CdSO_4.8H_2O$) and 0.3 gram of sodium hydroxide in 1 liter of distilled water.

Jacobs et al., emphasized the problem of the "oxidation" of sulfides by the relatively large volumes of air which were aspirated through an impinger and suggested that "oxidation" was minimized by using the alkaline cadmium hydroxide absorbing mixture. Recently, chemists of the Swedish Air and Water Laboratory (120) have reported that the zinc slurry is superior to the widely accepted cadmium hydroxide slurry. This report appears to contradict the earlier data of Jacobs, et al., and Marbach and Doty. Thus it appears necessary to re-examine the zinc absorbing solution in view of the recent improvement in the cadmium hydroxide slurry sampling technique (121).

Since the cadmium hydroxide slurry-methylene blue method for the determination of hydrogen sulfide is commonly used and Adams, et al. (122) were unable to obtain agreement between this method and the coulometric titration method, the former method was intensively investigated. This study revealed losses of 30-80 percent when collecting ppb concentrations of hydrogen sulfide in cadmium hydroxide suspension in midget impingers and determining the collected sulfide by methylene blue.

The methylene blue color development is dependent upon the formation of methylene blue from the reaction between sulfide and p-amino-N,N-dimethylaniline in the presence of ferric chloride. The molar absorptivity is reported to be about 34,000 in range of 5-50 μg $S^=$ per 100 ml, thus providing an exceptionally sensitive system. The color development is influenced by temperature, time and acidity. However, the colorimetric method is quite reproducible using ordinary laboratory precautions and was not related for the sulfide losses observed.

The possibility that the observed loss could be related to low collection efficiency had been eliminated by the work of Bostrom (123) wherein the collection efficiency for isotopic H_2S^* in cadmium hydroxide suspension was found to be in the range of 93-98 percent. The CdS^* collected in the absorption solution was oxidized to $S^*O_4^=$ with hydrogen peroxide in slightly acid solution. Unfortunately, the analytical method did not provide any information concerning the fate of the $S^{*=}$ during aspiration and storage, since analysis was based upon the amount of BaS^*O_4 precipitated from the $S^*O_4^=$ produced from the complete oxidation of CdS^*.

A review of the earlier literature showed that Marbach and Doty experienced the lowest sulfide losses when the cadmium was either completely precipitated with an equimolar addition of NaOH (pH 9.6) or when an excess of NaOH was present (pH 13.0). Marbach and Doty used the equivalent of 4.3 g of $3CdSO_4 \cdot 8H_2O$ and 1.3 g NaOH to prepare their fully precipitated $Cd(OH)_2$ sulfide collection media. Subsequently, Jacobs, et al, recommended only 0.3 g NaOH per liter (pH 7.5).

Since Jacobs, et al., did not discuss the reasoning behind their reduction of the 1:1 molar ratio of Cd/2NaOH--recommended earlier by Marbach and Doty--to the Jacobs ratio of 1:0.25, a series of Cd/2NaOH ratios between 1:0.25 and 1:1.3 were prepared to re-examine the influence of alkalinity. Samples of higher pH gave consistently higher sulfide recoveries, however, the improvement was not considered to be significant. Variable losses of 30-70 percent were observed over the pH range of 7.5 to 12.0.

Since Jacobs, et al., (95) had suggested that sulfide losses were caused by oxidation, replicated impingers containing 15 ml of $Cd(OH)_2$ suspension and added sulfide were purged with nitrogen, air, and oxygen. Sulfide losses were not significantly greater for the air and oxygen treatments than for the nitrogen treatment, indicating that the observed sulfide losses were not related to oxidation. However it was observed that the sulfide loss appeared to be related to the length of exposure to laboratory light. The data indicated a possible photodecomposition of the sulfide. A parallel study of a number of common antioxidants and protective colloids showed that sulfide collected in a cadmium hydroxide slurry containing 1 percent STRactan 10 (98) significantly improved the sulfide recovery in light and dark.

The modified cadmium hydroxide slurry with 1 percent added STRactan provides reasonable protection from photodecomposition. Recoveries are in the order of 80 percent ± 3 percent in the low parts per billion concentration range. This method has been field tested (124) and adopted as standard by the Bay Area Pollution Control District (99). An extensive evaluation of the effect of possible interfering compounds is underway and was reported during 1969 (125). The method is being considered for adoption by the Intersociety Committee.

Prescher and Lahmann (126) have also discussed the methylene blue colorimetric determination of hydrogen sulfide in ambient air. They concluded that methods available in 1966 for the determination of low concentrations of hydrogen sulfide were inadequate. The lead acetate and silver nitrate impregnated tapes were deemed neither sufficiently sensitive nor accurate. They recommended collecting hydrogen sulfide in cadmium hydroxide suspension in the dark from the moment of air intake until the analysis was accomplished. These authors also compared the Buck and Stratman (127) molybdenum blue method with the Mecklenburg and Rosenkranzer (128) methylene blue method for determination of hydrogen sulfide and concluded that the reaction of hydrogen sulfide with methylene blue produced a more intense color and was therefore to be preferred.

G. Fluorimetry

Andrew and Nichol (129) described a continuous analyzer for hydrogen sulfide. Hydrogen sulfide quenches the fluorescence of tetra-acetoxymercuri-fluorescein linearly between 5 ppb and 1 ppm. The short-term sensitivity of the instrument is approximately 5 ppb. This reagent appears to have useful application in a continuous, automatic colorimetric analyzer for H_2S. However, extensive studies would first be required to establish possible interferences from other air pollutants and to confirm the reported sensitivity.

H. Selective Ion Electrodes

At the present time more than 20 ion-selective electrodes are commercially available and several are being adapted for the continuous monitoring of flowing streams. Swartz and Light (130) have used three electrodes--fluoride, sulfide, and cyanide--as detectors for process monitoring instruments for use in the pulp and petroleum industries. There is insufficient evidence to establish the limits of sensitivity and hence the potential usefullness of the sulfide electrode for atmospheric monitoring, although considerable progress has been reported in the application of the fluoride electrode for atmospheric monitoring in the ppb concentration range in the vicinity of alumina reduction plants (131). A study of the possible application of the sulfide electrode for atmospheric monitoring is recommended.

9.2.5.3 Methyl Mercaptan

A. Colorimetric

The odor threshold for methyl mercaptan is reportedly in the range of 0.3-5 ppb (86, 87). Mercaptans in the air are absorbed in an aqueous solution of mercuric acetate-acetic acid in midget impingers (132).

The spectrophotometric method for mercaptans depends upon the reaction between N,N-dimethyl-p-phenylenediamine and mercaptan in dilute nitric acid and in the presence of ferric chloride (133). Moore, et al., (132) reported that hydrogen sulfide did not interfere when present in the range of 0-150 µg. Figure 9-1 compares the absorbance of the complexes produced by hydrogen sulfide, mercaptan, and alkyl disulfides with the "Jacobs" and "Moore" reagents.

From these absorbance curves it is apparent that (a) methyl mercaptan will interfere with the "Jacobs" colorimetric determination of H_2S by approximately 5 percent on a molar basis, (b) the potential interference from dimethyl disulfide in the Jacobs method is negligible, (c) hydrogen sulfide will not interfere with the "Moore" colorimetric determination of methyl mercaptan and (d) dimethyl disulfide will interfere with the "Moore" colorimetric method approximately mol for mol if retained in the impinger by the absorption solution. Fortunately, dimethyl disulfide is only partly retained in the mercuric acetate=acetic acid absorbing media and, therefore, is not a practical source of interference.

This method is intended for the determination of mercaptans in the range below 100 parts per billion. For concentration above 100 ppb the sampling period can be reduced or the liquid volume increased either before or after aspirating. The minimum detectable amount of methyl mercaptan is 0.04 µg per ml (86) in a final liquid volume of 25 ml. When sampling air at the maximum recommended rate of 1 liter per min. for 2 hours, the minimum detectable mercaptan concentration is 2.0 ppb (3.9 µg methyl mercaptan per cubic meter at 76 cm mercury and 25°C).

The N,N-dimethyl-p-phenylenediamine reaction is also suitable for the determination of other sulfur-containing compounds including hydrogen sulfide and dimethyl disulfide. The potential for interference from these latter compounds is especially important, since all of these compounds commonly coexist in certain industrial emissions. Appropriate selection of the sample collection and color formation conditions minimize the interference from hydrogen sulfide and dimethyl-disulfide.

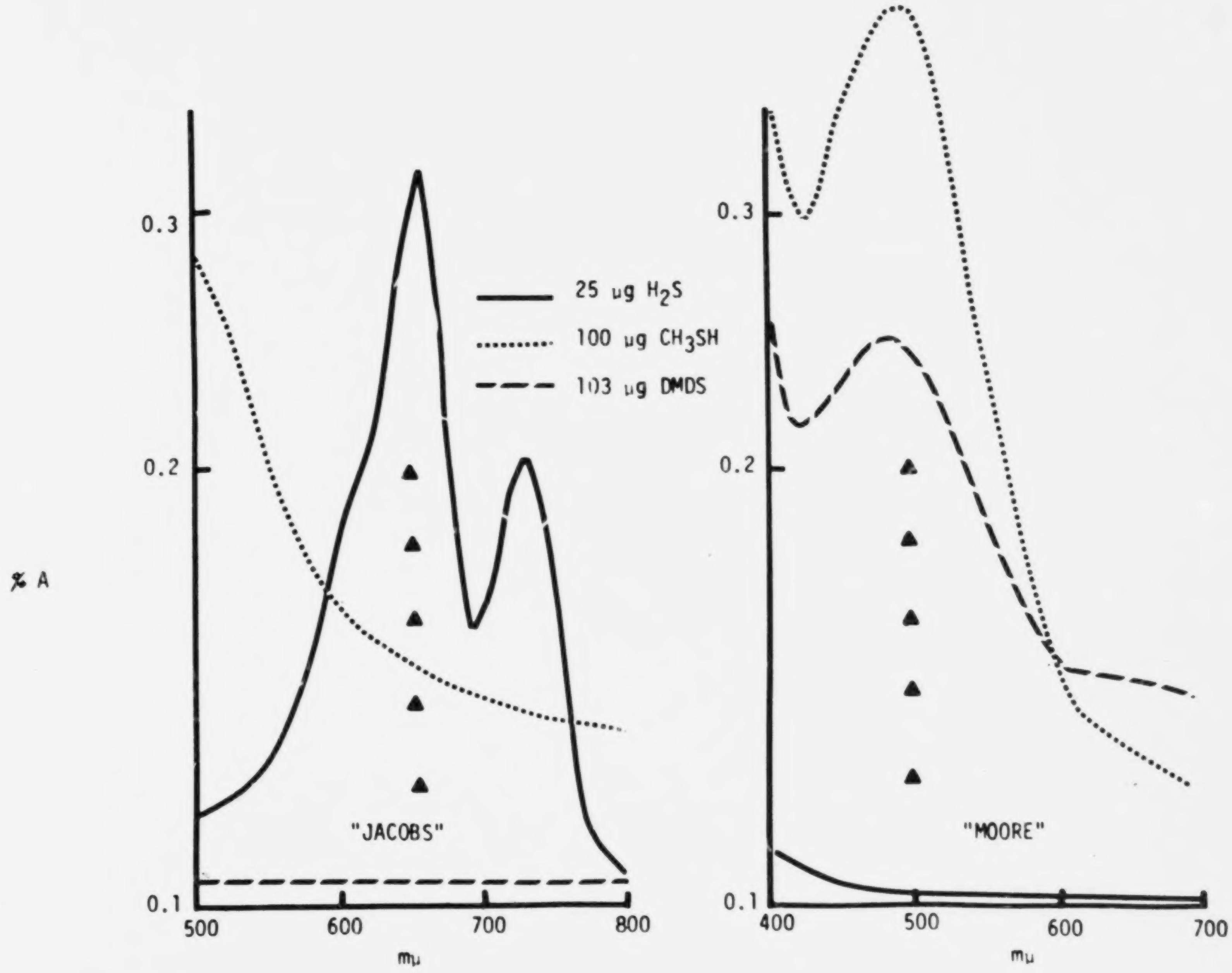

FIGURE 9-1. ABSORBANCE - "JACOBS" AND "MOORE" REAGENTS

Hydrogen sulfide, if present in the sampled air, may cause a turbidity in the sample absorbing solution. This precipitate must be filtered before proceeding with the analysis. One study showed that 100 μg H_2S gave a mercaptan color equivalent to 1.5-2.0 μg mercaptan (132) Another study reported no absorption at 500 mμ in the presence of 150 μg of hydrogen sulfide (136).

Approximately equimolar response is obtained from the hydrolysis products of dimethyl disulfide--the extinction coefficient for the amine-mercaptan reaction produce being 4.4 x 10^3 and for the amine-dimethyl disulfide reaction product being 5.16 x 10^3 (92). In practice, however, the collection efficiency for dimethyl disulfide in aqueous mercuric acetate is low and the actual interference is negligible. Sulfur dioxide up to 250 μg does not influence the color development even when sampling a test atmosphere containing 300 ppm SO_2.

Nitrogen dioxide does not interfere up to 700 μg NO_2 when sampling a test atmosphere at 6 ppm. Higher concentrations of NO_2 caused a positive interference when mercaptans were present but no interference in the absence of mercaptans.

The supply of mercuric acetate must be free of mercurous ion. If mercurous ion is present turbidity will result when the chloride ion-containing reagents are added in the last step of the analytical procedure.

The coefficient of variation for four mercaptans from methyl to hexyl mercaptan ranged from 0.0-2.6 percent (132). The coefficient of variation increased with increasing molecular weight of the mercaptans.

In several instances (133, 134) interferences have been reported from unknown compounds when using the method in the vicinity of kraft mills. In one of these, formation of a light-colored precipitate was reported. The apparent interference was not delivered due to emissions from the kraft mill since in most instances the wind was blowing from a nearby community toward the samples when the precipitate was noted. Cause of the problem is being investigated.

The method is being considered for adoption by the Intersociety Committee.

9.2.5.4 Alkyl Sulfides and Disulfides

A satisfactory analytical method for these compounds which is sensitive to concentrations usually found in the ambient air is not available at this time.

9.2.5.5 Sulfur-Containing Gases - Total or by Separation

A. Conductivity

Conductivity instrumentation, such as the Thomas Autometer (55), designed for monitoring sulfur dioxide by measuring the increase in electrolytic conductivity of a dilute hydrogen peroxide-sulfuric acid absorption media, can be used for hydrogen sulfide by first passing the air sample through an oxidizing furnace to convert the hydrogen sulfide to sulfur dioxide (138). The sample is then analyzed in the usual manner by continuous or batch conductivity measurements. If sulfur dioxide is also present in the atmosphere, correction must be made by simultaneous analysis of oxidized and unoxidized samples or by alternating a single air stream first through the furnace to the Autometer and then directly to the Autometer. This technique has not been used extensively because of the obvious equipment complications and the potential errors from many common interfering substances in the atmosphere which would either increase or decrease the reagent conductivity (139).

B. Coulometry

Coulometry is based upon the principle of electrically generating a selected titrant (ion or element) in a titration cell. The current required to generate sufficient titrant is a linear measure of the concentration of reactable compounds in the gas sample. In practice the titration cell has two sets of electrodes--a generating pair and a reference pair. A constant low level of titrant is continuously generated to produce a "zero level" on the instrument. When reactable compounds enter the cell the available titrant is reduced. The associated feedback amplifier responds to the change in sensed titrant level and generates sufficient additional titrant to maintain the "zero level" concentration. The additional generating current is related to the reactant by the following equation:

$$\text{Microequivalents} = \frac{\text{Q coulombs x } 10^{6}}{\text{(96,000 coulombs/equivalent)}}$$

The following equation is used to calculate the concentration of reactant when using a recorder of known characteristics to follow a coulometric titration:

$$\text{Microequivalents} = \frac{V \times S \times 6 \times 10^{-2} \times A \times 10^{6}}{R \times 96{,}500}$$

where V = mV/in. recorder sensitivity

R = ohms resistance of the coulometer range ohms switch

S = chart speed in min/in.

A = area under the titration curve, $in.^2$

Instrumentation for coulometric titration with electrolytically-generated bromine has been used for the determination of bromine-oxidizable sulfur gases (140). The Titrilog (22, 23) embodying this principle has a sensitivity of approximately 100 ppb. The sensitivity of the Titrilog was improved approximately 10-fold to 10 ppb by addition of a "R-C" network (141, 142).

The barton "Titron" Model 286 (25) represents a similar instrument using bromine coulometry and solid-state electronics.

This instrument has a limiting sensitivity of approximately 25 ppb H_2S. Thoen (27) has reported a 5 ppb sensitivity for a "total sulfur" in the ambient air with this instrument by substituting a Leeds and Northrup Model H recorder for the API recorder provided with the Barton 286.

Microtitration cells utilizing silver-silver chloride electrodes have been used for coulometric analysis of hydrogen sulfide and mercaptans (143). The cell will not respond to SO_2 or alkyl sulfides and disulfides. The sensitivity of this detector is reported to be approximately 100 ppb.

An iodine, microtitration cell (MCT) (41, 42) and a Dohrmann coulometer (144) have been used for the analysis of sulfur-containing pesticides which have first been separated by gas chromatography and then oxidized to SO_2 or reduced to H_2S in an appropriate furnace (138, 145, 149). This detector could also be used for the direct analysis of SO_2 in air. The sensitivity of this iodine microtitration cell is in the order of 100 ppb for direct atmospheric analysis. The cell response is relatively slow and the electrolyte is too short-lived for practical application.

The basic design of the iodine cell was modified and converted to bromine coulometry by Adams, et. al., (150). This microcell has an instantaneous sensitivity of approximately 3 ppb for hydrogen sulfide, which approaches the sensory detection threshold. The cell has been calibrated with permeation tubes (93).

Selective pre-filters have been developed for use in sequence ahead of the MCT cell to provide a separate analysis for sulfur dioxide, hydrogen sulfide, mercaptans, and alkyl sulfides and disulfides (151). Table 9-1 describes the series of preselective filters which provides the best compound separation.

The filters are preceded by an all plastic and stainless steel electrostatic precipitator to prevent build-up of particulates on the face of the impregnated membrane filters. The electrostatic filter must be operated at a sufficiently low voltage to prevent ozone production which would yield a negative response from the MCT.

The filters must be placed in the order shown in Table 9-1 for optimum results. When mercuric nitrate or silver nitrate is used to retain H_2S or CH_3SH, the nitric acid reaction product interferes with the MCT response. This interference is eliminated by using a bicarbonate backup filter.

TABLE 9-1

SELECTIVE FILTRATION SERIES-PERCENT RETENTION

	SO_2	H_2S	CH_3SH	DMS	DMDS
1. No filter	0	0	0	0	0
2. $NaHCO_3$	100	10	4	5	3
3. Lead acetate	100	100	4	5	5
4. Mercuric acetate	100	100	100	5	3
5. Hg acetate + tartaric acid and $NaHCO_3$	100	100	100	85	10
6. $AgNO_3+H_3BO_3$ + tartaric acid and $NaHCO_3$	100	100	100	100	100

In an automatic, sequential sampling system, air is sequentially sampled through a series of filters and then passed through the bromine MCT, thereby providing a stepwise recording of the concentrations of the various sulfur-containing gas fractions present in the air. A typical stepwise analysis for the five-gas mixture is shown in Figure 9-2. The pre-selective filter-bromine microcoulometric techniques and the STRactan-cadmium hydroxide-methylene blue techniques were compared in the field near a kraft pulp mill. Excellent agreement was obtained for hydrogen sulfide (152).

A study of the break-through or life expectancy of each of the five filters for five sulfur gas types has been completed (153). The data indicate that these filters have a useful life of at least 24 hours at concentrations well above those which have been observed in previous field studies. Additional work will be required to determine the possible effects of other common air pollutants on the pre-selective filters. The small plastic precipitator could be a source of contamination and possibly a maintenance problem. More work is needed to verify the separation of sulfur compounds in the presence of other non-sulfur compounds. Also, some work should be conducted to determine if there is a relationship between particulate matter and odor. Does particulate matter from the kraft process actually act as a carrier for malodorous compounds? If this is true, prefiltration of samples could give erroneous results.

C. Flame Photometry

A flame photometric detector (FPD) for the gas chromatographic analysis of sulfur and phosphorus compounds was described by Brody and Chaney (154). In its original application this detector was attached to the exhaust of a chromatographic column. The flame is viewed through selected optical filters (394 mμ for sulfur compounds) and the emission is sensed with a photomultiplier tube. Applications have been suggested for pesticide residue, air and water pollution process control, and natural gas (155).

Adams (156) suggested that "it should be possible to use this detector for the direct analysis of the atmosphere for total sulfur gases." Harding (157) reported varying detector response to CH_3SH and H_2S. The sensitivity of his detector appeared to be in the range of 50-100 ppb.

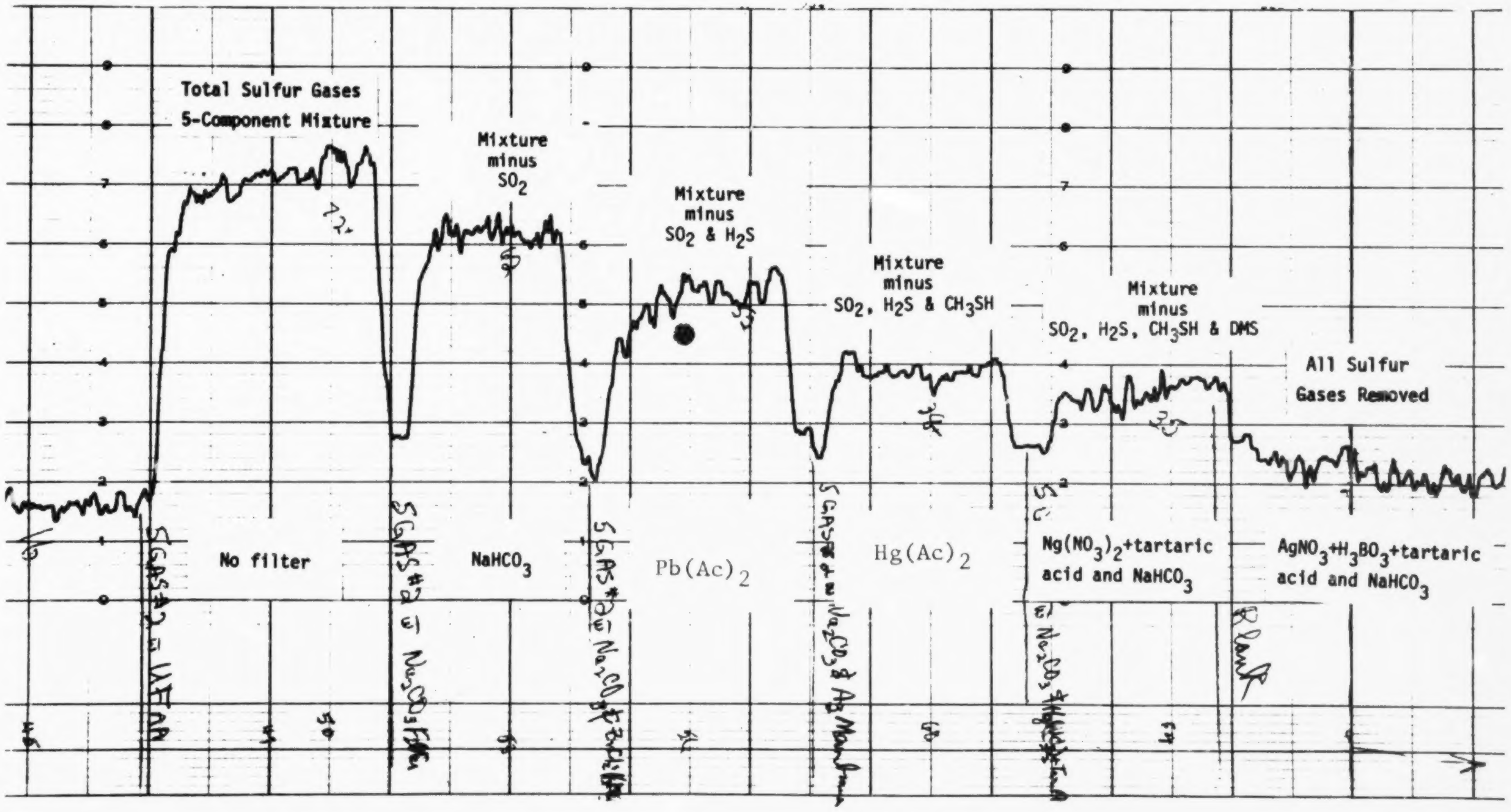

FIGURE 9-2. STEPWISE SEPARATION AND ANALYSIS OF 5-COMPONENT SULFUR-CONTAINING GAS MIXTURE

Approximately two years later, Stevens and co-workers (50) reported that an improved FPD could be used for the direct analysis of volatile sulfur compounds in the atmosphere. The continuously sampled air is passed through a hydrogen-rich flame which is viewed at 394 mμ by a photomultiplier tube. The detector has a reported specificity ratio for sulfur to non-sulfur compounds of 40,000:1 and a sensitivity to sulfur dioxide down to 5 ppb. Selective scrubber systems including aqueous and impregnated filters were used to remove quantitatively one or more of several sulfur compounds from atmospheric samples and thus make the detector more specific for an individual sulfur compound. This research is discussed in detail in the section on sampling and analysis of gases from sulfite mills.

D. Long Path Infrared

Intramolecular bonding may also be studied by infrared analysis techniques. This is probably the least sensitive of the techniques discussed. A multiple-reflection gas cell of 10-40 meters path length would have a sensitivity above the ppm level. The Franklin Institute 430 meter infrared gas cell used in the study of the complex photochemical reactions of the Los Angeles-type smog has a sensitivity of approximately 100 ppb and a price in excess of $25,000 (158). Infrared instrumentation is considered to be the least practical of the methods described for direct, automatic air analysis.

E. Plasma Source Emission Spectrometry

McCormack et al., (159) have reported a sensitive emission spectrometric detector with excellent selectivity for certain chemical bonds including C-S and C-N. This detector was successfully used by Bache and Lisk (160) for the gas chromatographic analysis of organo-phosphorous insecticide residues. Characteristic spectral lines for these and other organic bonds produced in a microwave-excited argon plasma are measured in the ultra violet light region using a grating spectrometer. Moye (161) increased the sensitivity of this detector. Specific instrumentation utilizing this detector is not commercially available.

An automatic instrument probably could be constructed using a relatively low-cost multi-channel quantometer-type spectrometer by substituting a microwave-excited argon plasma emission source for the usual spark or arc source.

The airborne sulfur-compounds would first have to be collected and concentrated in a liquid absorbant and then periodically injected into the argon plasma The concentration step is required to separate the sulfur compounds from air since the argon plasma will not form in the presence of air. The sensitivity of this technique for C-S bonds should approximate 200 ppb. if present for 30 minutes.

F. Gas Chromatography

Columns. The use of gas chromatography for the separation and determination of individual compounds from the kraft pulping process has progressed through several generations of detectors and column packing with ever increasing sensitivity and specificity since its first applications to the analysis of kraft source gases (162-164). Williams (165) used GLC analysis of ambient air samples to identify more than 30 organic compounds including dimethyl disulfide. The air sample was first dried by passing through a drying agent and then concentrated on a cooled, short section of stainless steel tubing packed with same column packing used for separation. The samples were later desorbed and analyzed with FID and EC detectors. Although detector technology provided dramatic improvements in sensitivity and compound specificity between 1957 and 1968, the direct analysis of ambient air concentrations of sulfur gases has been delayed by a lack of non-reactive partition liquids and column packings (166).

Stevens and co-workers (51) reported early in 1969, two techniques for the direct gas chromatographic analysis of sulfur gas mixtures in the low ppb range normally encountered in the ambient air. The first method involves the use of "differential response chromatography" (168). In this technique low concentrations of the sulfur gases to be determined are added to the chromatographic carrier gas by passing the carrier gas over appropriate permeation tubes (93) In this manner a frontal elution takes place and the eluate composition assumes a steady state value. Unknown samples introduced into the same column will emerge and generate signals corresponding in elution time to the minor component, but in magnitude and algebraic sign to the difference in concentration from the steady stream. Using this technique, Stevens, et al. achieved a chromatographic separation of the determination sulfur dioxide from other sulfur gases at levels as low as 20 ppb.

The second, and more useful, method involves the elimination of sorption or reaction in the chromatographic column and column packing. Empirical studies disclosed that polyphenyl ether coated at 5 percent on 30 - 40 mesh Teflon, and containing 0.05 percent phosphoric acid, permitted passage and separation of the highly reactiv sulfur-containing gases down to concentrations of 10 ppb.

Unfortunately this work has not been substantiated at the low levels by other investigators. Further work appears necessary to confirm this pioneering effort.

Thermal Conductivity. Neither hot wire nor thermister thermal conductivity (TC) cells had adequate sensitivity to detect compounds in the sub parts per million concentration range.

Flame-Ionization Detector. Later when the flame ionization detector (FID) was developed it became possible to obtain a direct quantitative determination of the hydrocarbon sulfur compounds present in kraft source gases without resort to prior sample concentration. The FID is extremely sensitive for the analysis of hydrocarbons. The detector response is proportional to the number of carbon atoms in the molecule. Unfortunately, this detector responds only weakly to inorganic sulfur compounds such as hydrogen sulfide and sulfur dioxide. Bellar, et al., (169) have studied the sensitivity limits of the FID for the direct analysis of hydrocarbons in the atmosphere. Feldstein, et al., (170) established a comparative response factor of 0.3 for methyl mercaptan as compared with methane. These two values indicate that the FID should have a limiting sensitivity of 12.5 ng. CH_3SH for direct atmospheric analysis.

Since the FID has a greater response for hydrocarbons than for sulfur-substituted compounds of equivalent carbon content, these compounds must be separated prior to FID analysis.

Using the FID, Thomas (171) found the usual methyl mercaptan and sulfides as well as n-propyl, isopropyl, and ethyl mercaptans and sulfides in blow and relief gases. Unfortunately, the FID does not respond to H_2S or SO_2 and shows even greater sensitivity for non-sulfur containing hydrocarbons.

Electron Capture. An obvious extension of this work was the application of the highly sensitive FID to the gas chromatographic analysis of ambient air for hydrocarbon sulfides as well as evaluation of the electron.capture (EC) detector for all sulfur-containing gases. Adams, et al., (172) reported on the sensitivity of these detectors for sulfur-containing compounds. The EC detector was unsatisfactory because of its loss of sensitivity when in contact with water vapor and its apparent temporary poisoning by methyl mercaptan.

Coulometric. Microcoulometric detectors (MCT) including silver-silver chloride (143), iodine (41, 42) and bromine (150) can be used in conjunction with a polyphenyl ether column (51) for the selective determination of sulfur-containing gases. The microbromine cell is the most sensitive of the three and responds to all of the major sulfur gas emissions from the kraft process, whereas the response of the silver-silver iodine cell is limited to mercaptans.

Eads and Cooper (167) have reported that "odor producing sulfur compounds . . . including sulfur dioxide, have been detected at very low levels. . .by modifying a chromatograph coupled to a microcoulometer." The primary difference between this system and those previously reported by others (51, 166) appears to be in the use of a sample concentration step wherein the air is drawn through an impinger containing methanol. The introduction of a sample concentrating step wherein the absorbing media must be "measured, weighed and proper microliter quantities of methanol then injected into the system" appears to overly complicate the technique without achieving any greater sensitivity than is presently possible. Even the claimed sensitivity is subject to question since the GC column was 10 percent Triton X-305 on Fluoroport T which has previously been shown to retain appreciable quantities of sulfur-containing compounds (51).

Flame Photometric Detector. An improved Brody-Chaney flame photometric detector (FPD) (154) which is highly sensitive and specific for sulfur containing compounds at 394 mμ, was used by Stevens, et al., (51) in both methods for "direct" and "differential" analysis of sulfur compounds in the atmosphere.

This detector has a linear response over a concentration range from 10 ppb to 10 ppm. Stevens reports that the direct chromatographic technique has been automated and that air samples are periodically obtained with a rotating 6-port valve. Their present objective is to determine the ratio of sulfur dioxide to other sulfur containing gases in the atmospheres of urban and pulp mill environments.

The FPD must still be subjected to a critical evaluation of the possible interference from other air pollutants.

Solid-State Electrochemical Detectors. Bechtold (173) used the solid-state electrochemical cell Pt/Ag/AgI/Ag_2S/Pt to measure concentration changes in sulfur- and halogen-containing compounds in a carrier gas stream. Sulfur and halogen compounds were first oxidized in a combustion furnace containing platinum at 800°C and then passed over the electrode surface within an operating temperature range of 200 - 420° C. The electrode response was linear over at least four orders of magnitude and had a detection limit of approximately 1 nanogram for CS_2. Detector response was not affected by overloading.

This electrode was initially used as a gas chromatographic detector for pesticide analysis. Because of its sensitivity and specificity, this electrode has a potential use as a continuous detector for total atmospheric sulfur gases, or as a stepwise sulfur compound class analyzer using preselective filters. Because the detector is solid-state, the problems associated with conventional coulometric detectors having liquid electrolytes will be eliminated. However, other problems may develop under the application proposed above.

9.2.5.6 Sulfur Dioxide

Both continuous and batch sampling methods are available for sulfur dioxide concentrations which are experienced in the ambient air. These will be discussed in detail in Section 9.3.4.

9.2.6 AMBIENT SAMPLING (PARTICULATES)

9.2.6.1 Dustfall

This technique is intended for the collection of settleable particulates from the atmosphere and the subsequent characterization of the collected material (70, 174, 176). ASTM, APCA, and NCASI have similar methods for this technique. Particulate material which is of a particle size and density which will settle by gravity into an open-top container is usually collected over a 28-day or one-month period. The container and contents is then transported to the laboratory for weighing and analysis. The analytical procedures which are most frequently used in evaluating the collected material in the vicinity of kraft pulp mills include the determination of pH, total weight, total water-soluble and benzene-soluble material, total volatile and non-volatile matter, sodium, calcium, sulfate, and chlorides. When dustfall is sampled and analyzed over an extended period of time and from an adequate number of representative sampling sites the relative contribution of settleable material from a kraft pulping operation and other segments of the community activities can readily be seen from monthly isopleths of each measured component or characteristic of the dustfall. A typical evaluation of the relative contribution of a kraft mill and the community to dustfall was reported by Adams and Koppe (175). Isopleths of the average values for 15 sampling sites for each of 13 components determined in the collected dustfall revealed the existence of several significantly different fallout patterns. Similar patterns were found for sodium, sulfate, soluble solids, ash, and pH. Different patterns were observed for ammonia, nitrates, calcium, insolubles, insoluble ash, loss on ignition, phosphate, and chloride. Duncan (70) has provided a comprehensive description of the manner in which to establish a dustfall survey within a kraft mill community.

Studies on the influence of the design of dustfall collectors have been reported by several groups of investigators. It now appears that dry bottom plastic collector is entirely satisfactory (176). Elimination of water or antifreeze from the collector has greatly simplified the procedure for agencies or companies maintaining a number of collectors over a relatively large area. However, it is recommended that in areas where more than one agency is maintaining a dustfall network, all collectors be of a uniform nature to permit intercomparison of data. It is further recommended that agencies establishing new networks utilize the latest Intersociety Committee, ASTM, or APCA Standards, in that order, when they are available. This is a field method of long standing.

9.2.6.2 Suspended Particulates

This method is intended for the collection of fine particulates between 0.3 and 50-100 microns (177). A large volume of air (40,000-75,000 ft^3) is drawn through the fibrous filter for a period of time such as 24 hours. The filter is weighed under controlled temperature and humidity conditions before and after use and the difference in weight is reported as micrograms per cubic meter of air sampled. The "hi-vol" samplers and shelters designed to prevent collection of particles larger than approximately 100 microns are well known and extensively used by the National Air Sampling Network of NAPCA (177). Two comprehensive reviews relative to the use of the hi-vol sampler to kraft mill air pollution problems have been published by the National Council for Air and Stream Improvement (70, 178). These are field methods.

Committee TR-2 of the Air Pollution Control Association has recommended a "Standard Method for Atmospheric Sampling of Fine Particulate Matter by Filter Media-High Volume Sampler" (179). The standard describes suitable instrumentation, instrumentation housing, and analytical procedures to be used for characterization of the collected particulates.

In addition to the determination of the total weight of suspended particulates collected, portions of the filter may be analyzed for sulfate, sodium, calcium, and benzene solubles. Other analyses may be performed if the objective is to determine the relative contribution from a kraft mill as compared with other community sources.

Scaringelli and co-workers (180) have devised a fractional decomposition technique wherein sulfuric acid aerosol and alkali sulfates are separated from concomitantly present heavy metal sulfates on a high volume filter. The volatized sulfates are passed over copper gauze and the sulfates reduced to SO_2. The resultant SO_2 is determined by iodine MCT.

9.2.6.3 Sticky Paper

Various sticky coatings, including vaseline, dilute rubber cement, gelatin, glycerine jelly, and Scotch tape have been exposed to collect atmospheric particulates. Pritchard, et al., (181) evaluated several gum rubber label stocks as impingement media for collecting wind blown atmospheric dusts. Field evaluation of 37 adhesive-coated materials indicated that Fasson R-135 was best suited for particle collection. In practice the sticky tape is placed on a vertically mounted cylinder and the north direction of the tape marked for orientation. Following exposure for one week the tape is returned to the laboratory for examination, counting and identification by known microscopic techniques (182).

9.2.6.4 Visual Range

The Charlson-Ahlquist visual range nephelometer is a light scattering device which is finding increased application in the continuous recording of the variations in meteorological range at the sampling site (183). The scattering coefficient (meter^{-1}) thus derived can be related to meteorological range and to the mass of aerosol per volume of air. The correlation between meteorological range as determined by the nephelometer and the mass loading as determined by the hi-vol sampler has been found to be above +0.9 in widely separated urban areas such as Seattle, San Jose, and New York City (184). When the atmospheric humidity exceeds 70% the correlation between the nephelometer and mass loading decreases.

Further evaluation of the nephelometer under a variety of urban, industrial, and rural conditions will be required to further substantiate its usefulness in the characterization of atmospheric particulates. The nephelometer is non-specific and responds to particulates from all sources present in the environment.

9.2.7 RECOMMENDED AMBIENT METHODS

9.2.7.1 Gaseous Sampling and Analysis

A. Sensory

Use the Scentometer (105) as an aid in conducting subjective odor evaluation studies in place of an arbitrary odor intensity scale.

B. Wet Chemical

Hydrogen Sulfide. Sample air at 1 liter per minute using a midget impinger containing cadmium hydroxide slurry and 1 percent STRactan 10 (121). Protect the impinger(s) from light by wrapping with black paper or electrician's tape. Determine the collected sulfide by the methylene blue procedure (95, 118) within 24 hours if possible.

Methyl Mercaptan. Sample air at 1 liter per minute using a midget impinger containing mercuric acetate solution. Determine the collected mercaptans spectrophotometrically by reaction with N, N-dimethyl-p-phenylenediamine (132, 135).

Dimethyl Sulfide and Dimethyl Disulfide. There are no sufficiently sensitive wet chemical methods for determination of these compounds in the ambient air.

Sulfur Dioxide. See Section 9.3.6

Gas Chromatography. A polyphenyl ether-Teflon column will separate complex mixtures of volatile sulfur gases down to approximately 5 ppb (168). Detection of the separated compounds can be accomplished at this concentration range with either the FPD (154) or the bromine MCT (150). The gas chromatographic method has been automated to provide sequential analyses at 10 - 15 minute intervals (51).

Pre-Selective Filtration. Chemically impregnated membrane filters provide separation of the five major volatile sulfur gases found in the vicinity of kraft pulp mills (152). Detection of the fractionated samples may be accomplished with either the bromine MCT (151) or the FPD (154).

Total Volatile Sulfur Gases. Either the bromine MCT (151) or the FPD (51) can be used to provide a continuous real-time determination of atmospheric fluctuations of these gases. Both detectors will require a minimum of daily attention to assure maximum operating reliability.

9.2.7.2 Particulate Sampling and Analysis

Dustfall. Dry bottom containers with adequate bird rings are useful in examining 4-week or 30-day accumulations of settleable particulates. Selected chemical analyses can provide information on possible sources of the collected material (70, 174, 176).

Suspended Particulates. Hi-vol sample filters can be analyzed to provide information concerning possible sources of suspended particulates (70, 178, 179).

Sticky Paper (181). Microscopic examination of sticky paper can provide information on the nature of particles collected and the direction from which they came.

9.3 SULFITE SOURCES

The gaseous emission of principle interest in the sulfite process is sulfur dioxide. The nature of particulate emissions depends upon the cooking base and whether recovery by burning is practiced.

9.3.1 SOURCE SAMPLING (GASES)

9.3.1.1 Continuous Monitoring

Three methods have been used to monitor sulfur dioxide from the sulfite process. These methods include infrared and ultraviolet spectroscopy and conductivity.

Non-dispersive infrared analyzer (185) has been used in a magnesium base acid bisulfite mill with success. The reference cell contained all of the flue gas components less the sulfur dioxide. The flue gas is passed through the sample cell at 3.5 CFH and the differential output is related to the SO_2 in the flue gas. The IR cell windows must be protected from water. In one instance, a large filter is followed by a refrigerated dryer reducing the flue gas to -10°F. Particulates in the flue gas caused frequent plugging of the sample line and the instrument environment was unduly corrosive for the electronic circuitry. It is estimated that one installation cost in excess of $10,500 and has been continually plagued with approximately 50 percent instrument downtime.

Thoen's ultraviolet system (186) by contrast is quite simple in design, relatively inexpensive (less than $2,000), and extremely reliable. The ultraviolet source and detector are mounted externally to the flue gas duct and protected from the flue gas by quartz windows. A 2 1/2 inch diameter tube is located at 90° to the flue gas flow and connects the externally mounted source and detector. One-half inch holes are placed 2 1/2 inches apart at 90° to the gas flow. These physical arrangements minimize particulate and water accumulation in the light path tube. Maintenance is limited primarily to a cleaning of the quartz windows every three weeks. The instrument has been calibrated externally to the flue gas duct by passing nitrogen-sulfur dioxide mixtures through the light path tube. (Possibly a more reliable calibration procedure would involve the addition of known quantities of sulfur dioxide to a flue gas matrix rather than the nitrogen gas base which has been used.) This work has not been confirmed by others.

A variety of conductivity instruments from home-builts to modified commercial units have been successfully used by several sulfite mills (187, 188). Conductivity units require close control of reagent and sample gas flow to maintain calibration. These instruments are relatively inexpensive.

Correlation spectrometry and multiple-scan interferometry (189 - 191) have been proposed for use as remote sensing devices to determine the SO_2 concentration from industrial and power plant stacks. In theory the instrument could be used by the emitter at the source to monitor SO_2 emissions or by regulatory officials located in a mobile unit at some distance from the source. Significantly, this can also be done at night. This instrumentation is considerably more complex than Thoen's ultraviolet system. Thus initial expense and subsequent maintenance could be significantly greater.

9.3.1.2 Batch Sampling

A large number of methods has been published. Some methods such as the hydrogen peroxide titration method will include all of the sulfur trioxide. The sample is drawn through an impinger containing dilute hydrogen peroxide. The sulfuric acid formed is titrated with standard sodium hydroxide solution using a mixed indicator of bromocresol green and methyl red (192).

In the iodine thiosulfate method, the sample is drawn through a standard solution of iodine in potassium iodide, the iodine remaining is then determined by titration with standard thiosulfate solution (193). A major source of error is the loss of iodine from the impinger containing the iodine - KI solution. A second impinger in series containing standard thiosulfate solution is used to collect any iodine carried over from the first impinger.

9.3.2 SOURCE SAMPLING (PARTICULATES)

9.3.2.1 Continuous Monitoring

Particulate loading in kraft flue gases has been determined by continuously measuring the sodium ion concentrations in a stream of liquid which has scrubbed the flue gas sample. Leonard (194) has described a home-built analyzer in which a dilute ammonia solution is injected at the end of a sample probe. The particulates are removed from the flue gas sample by the liquid as the sample is drawn to the detector. The sodium concentration is measured with a sodium ion selective electrode. The instrument is calibrated against aqueous standards containing known concentrations of sodium ions. The technique may be applicable where recovery of sodium-base sulfite liquors is practiced.

Tretter (195), and Rivers and Neuberger (196) reported the use of a Chemonoitor® in a similar manner. In this application a Calgon buffer reagent is used instead of Leonard's dilute ammonia reagent. It is planned to substitue a steam eductor for the sample air pump and to back-flush the probe automatically every eight hours to eliminate problems of electrode fouling and probe plugging. The technique may be applicable where recovery of sodium-base sulfite liquors is practiced.

The bolometer which has been used for many years to measure smoke density and more recently to monitor particulate loading in kraft mill recovery furnace stack emissions (197) might be equally effective in recording total particulate loadings in sulfite mill emissions when properly calibrated and maintained.

Laxton and Lawton (198) have described an automatic monitor for recording sulfur trioxide in flue gas. The collected sulfate is reacted with barium chloranilate in 80 percent isopropyl alcohol in a continuous colorimetric recording system. The monitor has an upper limit of 50 - 100 ppm SO_3.

9.3.2.2 Batch Sampling

Fielder, et al., (199) sampled flue gas through a heated stainless steel probe containing glass wool. The flue gas is saturated with cold 80 percent isopropyl alcohol. A sulfuric acid mist is formed and collected on a sintered glass filter. The collected acid mist is washed off the filter and the sulfate determined turbidimetrically. The gases pass through the filter, are collected in an iodine-potassium iodide solution, and the SO_2 determined iodimetrically.

A similar sampling train was developed by M. Hissink (200) by collecting sulfuric acid aerosol on a heated glass filter cone kept at 200 - 250°F which is between the dew point of sulfuric acid and water. The SO_2 passes through the filter and is collected in a water scrubber.

Mader, et al., (201) filtered the sample through filter papers, specially prepared by leaching with distilled water and then dried, to trap the sulfuric acid aerosol. The acidity was determined by titration. Sulfur dioxide reportedly did not interfere.

9.3.3 RECOMMENDED SOURCE METHODS

9.3.3.1 Gaseous Sampling and Analysis

The ultraviolet and conductivity procedures have been most successfully used in the mill. The ultraviolet (186) instrumentation is less complex and it is not necessary to replenish reagents or control reagent flow or gas sampling rate. These latter methods appear to be the methods of choice.

Batch sampling requires a considerable expenditure of manhours to obtain intermittant data of limited value for process control. Non-dispersive infrared and interference or correlation spectrometric instruments are much more expensive and complex than are needed to monitor SO_2 emissions.

9.3.3.2 Particulate Sampling and Analysis

Measurement of particulate loading where recovery of sodium-base sulfite liquor is practiced is most readily accomplished by continuously measuring the sodium ion concentration (activity) in a continuous flow scrubbing system using an ion-selective electrode. The bolometer has not had adequate mill use. Its calibration to provide direct readout in terms of soda loss would be more difficult than with the ion selective ion electrode technique.

Methods for other particulate sources in sulfite mills have not been standardized.

9.3.4 AMBIENT SAMPLING (GASES)

Methods used for measuring sulfur dioxide may be classified into three categories: continuous monitoring, short-term batch, and cumulative. Each category provides a different type of information required in each given situation.

9.3.4.1 Continuous Monitoring

The most commonly used monitoring system is exemplified by the Thomas Autometer (202) which embodies the measurement of changes in the conductivity of the reagent due to the absorption of pollutants, assumed to be primarily sulfur dioxide, from the sampled air and interpreted in terms of equivalent sulfur dioxide concentrations. The sensitivity of these devices generally averages 0.05 ppm; however, they are non-specific, responding to any material which is collected by the absorbing solution and which will alter the conductivity of the absorbing solution. Fortunately, in most practical field situations, sulfur dioxide may represent the major polluting constituent or the solubility or collection efficiency of the scrubber may be significantly lower for other pollutants. Numerous field comparisons have been conducted which indicate that conductivity and other SO_2 procedures agree fairly well (203, 204), although the observed difference may be either positive or negative depending upon the characteristics of the indigenous air pollution. HCl, NH_3, and Cl_2 give particularly significant positive recorder responses. Shikiya and McPhee (205) foun unexplained differences from two- to four-fold between conductivity analyzers and between conductivity and colorimetric analyzers. Terabe, et al., (206) found that the conductivity method gave higher SO_2 values than the colorimetric method in Kawasaki, Japan.

More recently other continuous monitoring methods for SO_2 have become available including coulometry, colorimetry, flame photometry, and permeation into an electrochemical cell. The earliest available continuous coulometric analyzer, the Titrilog (22, 207), originally lacked the sensitivity and specificity required for monitoring the ambient air. Nader and Dolphin (208) and McKee and Rolliwitz (209) suggested modifications to improve the sensitivity; however, the method is not specific since any compound which can be oxidized by bromine will be interpreted as equivalent sulfur dioxide. The Titrilog II (23) has recently been introduced and is reported to have a minimum sensitivity of 0.02 ppm SO_2. The instrument response time is not stated in the instrument brochure.

Philips Industries (210) has also introduced a new coulometric analyzer. Their specifications indicate a standard full scale sensitivity of 1.15 ppm SO_2 with a possibility for achieving 0.115 ppm full scale sensitivity. The reported response time is 1.5 minutes to 63 percent of final value and 3 minutes to 95 percent of final value. The instrument is provided with a built-in SO_2 calibration source which may represent the first SO_2 instrument which can automatically provide a total instrument calibration. Beckman's (211) coulometric instrument is reported to have a very slow response time (212).

A bromine coulometric microtitration cell and selective pre-filters has been used in the laboratory and field for the analysis of sulfur-containing gases (150, 151, 213). Appropriate selection of chemically-impregnated membrane filters will permit measurement of the total sulfur-containing gases in the atmosphere and determination of the SO_2 levels by difference between total sulfur gas and total minus SO_2. Electrolyte in the microtitration cell is automatically replaced to maintain a drift-free condition. A sensitivity of 0.01 ppm SO_2 can be achieved and the response time for 90 percent of final value is attained in 15 - seconds.

The performance chacteristics of twelve commercially available (as of September 1, 1967) continuous sulfur dioxide monitors were determined by Rodes, et al. (214). Instruments based upon conductivity, colorimetry and coulometry were examined to determine such instrument characteristics as stability, sensitivity, response time, collection efficiency and response to interfering substances. Other, less extensive, instrument evaluations have been reported by Potter (212) and Givens, et al., (215). These studies have provided invaluable insight into the limits of application of these instruments. Certain instrument models have since been modified to improve certain shortcomings as revealed by these comparative tests.

In addition to the instruments reported in these studies, a number of new instruments have been reported or become commercially available within the past two years.

The flame photometric detector (FPD) (216) has been incorporated into a continuous sulfur gas analyzer (217) which will respond not only to SO_2, but also to H_2S and possibly mercaptans and alkyl sulfides and disulfides. Stevens, et al., have utilized the FPD in conjunction with gas chromatography (50, 51) to provide a separation of SO_2 from H_2S.

The automated colorimetric analyzers (218-220) provide delayed data output for sequenced sampling periods and therefore would not be adequate to establish compliance with an air quality standard involving 3-minute maximum allowable concentrations. These instruments would, however, provide suitable information for longer averaging periods of 15 minutes or more where additional delays of 15 - 30 minutes for completion of the analysis can be tolerated. The automated chemical procedures required, will most certainly increase the required maintenance and provide additional variables which must be accurately controlled if reasonable data are to be obtained.

Specially designed electrochemical cells separated from the sample air stream by a thin plastic film have been developed which appear to be relatively selective for SO_2, NO_2, and NO_x (221). Two versions of the SO_2 monitor provide for analysis of a maximum of 2 - 10 ppm or 1000 ppm SO_2. Initial laboratory evaluation of the low SO_2 monitor indicated that the full-scale sensitivity could be adjusted to 1 ppm SO_2. Interference from O_3, NO_2, Cl_2, H_2S, CH_3SH, RSR, and RSSR was either negligible or nonexistent within reasonable ranges of concentration.

Since the SO_2 enters the electrochemical reaction cell by permeation through the thin plastic membrane, the response of this detector is independent of a sample gas flow rate in the range of 1 - 3 CFH. Thus instrument maintenance should be limited in most instances to the manufacturer's recommended replacement of the sealed electrochemical reaction cell once every three months. Insufficient time has elapsed since the introduction of the instrument to permit adequate laboratory and field evaluation.

Selection of the continuous SO_2 analyzer to be used for ambient studies in the vicinity of a sulfite mill must be based upon a careful evaluation of the characteristics of the available instruments, the location of other sources of interfering compounds in the locality, and the requirements of the local air quality regulations. If the regulatory agency requires hourly or 24-hourly averages, then rapid response time is not a critical characteristic. If, on the other hand, a regulation states that a three-minute peak in excess of 1.51 ppm constitutes a violation, the Bay Area finds that instruments must provide a 75 percent of scale response to 2 ppm SO_2 for at least 1.75 minutes of a three-minute exposure at 2 ppm (212).

Data obtained with the non-specific analyzers described in this section must be interpreted with extreme caution because of the possible presence of interfering substances.

Instrument maintenance and reliability varies greatly from one instrument to another. With the newer instruments either limited or no field experience has been developed and no comparative testing has been reported to indicate how they compare with methods already in use.

9.3.4.2 Short Term Batch

The modified West-Gaeke (222) colorimetric method has gained the widest acceptance for either grab or sequential sampling for periods of ten minutes to 24 hours. Sulfur dioxide is collected in 0.1 M sodium tetrachloromercurate (II). The colorimetric determination is based upon the measurement of the red-violet color produced by the reaction of dichlorosulfitomercurate (II) with hydrochloric acid-pararosaniline and formaldehyde. Modifications have been developed to eliminate interference from oxidant (223), nitrogen dioxide (224, 225) and heavy metal ions (226). The method has been adopted as tentative by the Intersociety Committee on Methods for Ambient Air Sampling and Analysis (227).

Other short-term methods include (a) collection in dilute hydrogen peroxide-sulfuric acid solution and measurement of the change in conductivity, (b) collection in dilute hydrogen peroxide solution and titrimetric determination of the acidity, or turbidimetric or gravimetric determination of the resultant sulfate, and (c) collection in iodine-iodide and titration with standard thiosulfate solution. These latter methods are either not sufficiently sensitive or too time consuming to be used routinely for determination of sulfur dioxide in the ambient air.

Stratmann (228) described a method wherein SO_2 was first sorbed on silica gel. After sampling a known volume of air, the SO_2 was then desorbed and reduced to H_2S at 700 - 900° C in contact with a platinum catalyst. The H_2S was then absorbed in a 2 percent solution of ammonium molybdate and the equivalent sulfur dioxide determined colorimetrically. The method is fairly specific for SO_2, but the final determination of the resulting H_2S by molybdenum complex is not the most sensitive procedure available.

Pate, et al., (229) sampled concentrations of SO_2 by filtering air samples through potassium bicarbonate-impregnated types HA and AA Millipore^{P} filters. The filters were then analyzed for collected sulfate. The duration of the sampling period would determine whether the technique would be classified as "short-term batch" or "cumulative." The technique can provide air concentrations of SO_2 if the air sample volume is measured. Such quantification is not possible with static samplers such as the lead peroxide candle and Huey sulfation plate.

9.3.4.3 Cumulative Methods

The lead peroxide candle was developed in England by Wilsdon and McConnell (230) in 1932 as an inexpensive method for measuring the relative "sulfation" of the atmosphere at numerous selected sampling sites within a prescribed study area. Numerous investigators have reported varying relationships between sulfation and sulfur dioxide concentration in parts per million as a mean of the sulfur dioxide concentration over the period of the peroxide candle exposure. The method will not, however, provide short-term concentration data because of its relative insensitivity.

Huey (231) has developed a more convenient procedure which utilizes an inverted 48 mm Petri dish containing the lead peroxide paste. This technique eliminated the tedious job of coating the 100 square centimeter gauze surface used in the candle technique. A simplified Petri dish holder-bracket may be attached to a convenient utility pole, thus eliminating the square or round louvered shelters used with the candle. The performance of the plates was compared with the candles at several different locations. The plates were approximately 20 percent more reactive than the candles (231).

Harding and Kelley (232) used a 44-station network of 3 x 4 inch mild steel plates to demonstrate monthly corrosion patterns. The dispersion pattern of corrosion gave a reasonably good description of the SO_2 dispersion from several nearby sources. The correlation coefficient between sulfation and corrosion was 0.60, indicating that less than half of the variance could be accounted for by the relation to sulfation. Sea salt gave high corrosion rates near the Jacksonville beach, but dropped off to background within one mile from the beach.

9.3.5 AMBIENT SAMPLING (PARTICULATES)

9.3.5.1 Sulfur Trioxide

There is no satisfactory specific method for this material. Generally, available methods depend upon collection of the aerosol by filtration, electrostatic precipitation, or impaction (233). Subsequent interference by sulfur-containing gases may occur particularly in filtration. The collected material is then subsequently analyzed by determination of acidity of the sample, determination of the sulfate ion, or determination of the resulting conductivity charge. All of these techniques are subject to interference from other acidic materials, other sulfate salts, or all ionic pollutants.

Thomas, et al., (234) developed an automatic, non-specific method wherein the aerosol is collected by sonic impaction and the collected acid is determined with a conductivity cell. The air sample was then scrubbed through dilute sulfuric acid-hydrogen peroxide reagent and "SO_2" determined with a second conductivity cell. The method measures only the "effective" hydrogen ion concentration and is subject to potential positive and negative interferences.

Scaringelli and Rehme (235) developed a method wherein aerosols are separated from gases by impaction or filtration. The collected sulfuric acid aerosol is then decomposed at controlled temperature under a stream of nitrogen to separate sulfur trioxide from collected sulfates. The sulfur trioxide is converted to sulfur dioxide by reaction with hot copper. The sulfur dioxide is then collected and determined either spectrophotometrically, coulometrically, or flame photometrically. Ammonium sulfate is the only known compound which reacts similarly, but it is assumed that ammonium sulfate is formed in the atmosphere by the reaction of sulfuric acid and gaseous ammonia. The method is reported to be sensitive to sulfur trioxide in the parts per billion range with samples of only one liter of air.

Two visual methods have been proposed. Gerhard and Johnstone (236) impinged the air stream on an acid-base dye-impregnated film and measured the area of the resulting yellow spots. Lodge, et al., (237) microscopically examined and counted characteristic spots resulting from the impingement of the aerosols on a film of silicon monoxide supported on a Formvar impingement plate which was subsequently shadowed with cadmium or chromium. Both methods involve considerable manual labor in the microscopic evaluation of the film or plate. The Lodge procedure undoubtedly provides the most specific method available for detection and identification of sulfuric acid aerosol. Unfortunately, the method is limited to qualitative examination of aerosols to determine whether sulfuric acid aerosol is present and to provide an estimate of the ratio of sulfuric acid aerosol to other particulates in small volumes of air.

9.3.6 RECOMMENDED AMBIENT METHODS

9.3.6.1 Gaseous Sampling and Analysis

Continuous Analysis. At the present state of the art, conductivity and possibly the Titrilog II (23) offers the best reliability for the field monitoring of SO_2 in ambient air. Serious interferences may be encountered, however, in using these instruments.

Batch Sampling. Sample air at 1 liter per minute using a midget impinger containing sodium tetrachloromercurate (II) solution. Determine the collected by reaction with acid bleached pararosaniline following the Intersociety Committee Tentative Procedure (227).

Cumulative Sampling. The Huey sulfation plates (231) are recommended for use in any new survey. The British "candle" has been in use for many years and comparative data should be obtained by both techniques before abandonment of the "candle" is contemplated in an area where considerable historic data has been accumulated with "candles."

9.3.6.2 Particulate Sampling and Analysis

Continuous Analysis. The Thomas sulfuric acid aerosol impactor (234) and conductometric determination of the collected aerosol represents the only known method. The data obtained must be carefully evaluated considering the non-specificity of the method.

Batch Sampling. Impaction, filtration, and electrostatic precipitation may be used to collect samples for up to 24 hours. There is no satisfactory method for the determination of the collected sulfuric acid aerosols. Conductivity yields "effective" hydrogen ion. Gravimetric or colorimetric determination of total sulfate will include other soluble sulfates such as sodium and ammonium sulfate. Coulometric analysis of the pyrolyzed sample provide probably the best method for the determination of sulfuric acid (235), although titrimetric determination is much less complex.

9.4 NSSC SOURCES

No unique or special conditions apply to emissions from NSSC mills. It is believed that methods already discussed in previous sections will be adequate when applied to NSSC.

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CHAPTER 10

ON-GOING RESEARCH RELATED TO REDUCTION OF EMISSIONS

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CHAPTER 10

ON-GOING RESEARCH RELATED TO REDUCTION OF EMISSIONS

SUMMARY

A number of the problems facing the chemical wood pulping industry with respect to air quality improvement cannot be resolved until further research points the way.

A search of the technical literature for the past five years was undertaken. With few exceptions, it was decided that work reported more than five years ago was presently incorporated into practice, was under further development, or was found unsuitable for practical application.

The format selected for presentation was that of an annotated bibliography insofar as possible. Eight major categories were selected for presentation of the abstracts. Within each major category the abstracts are arranged in sub-categories by year of publication.

10.1 INTRODUCTION

A number of the problems facing the chemical wood pulping industry with respect to air quality improvement cannot be resolved until further research points the way. Answers to other problems are becoming clearer as a result of research presently underway. Since one of the main objectives of this study was identification of needed research, a survey of on-going research was a logical starting point.

A search of the technical literature for the past five years was undertaken. With few exceptions, it was decided that work reported more than five years ago was presently incorporated into practice, was under further development, or was found unsuitable for practical application. In addition to the published literature researchers known to be active in the field were contacted directly and NCASI provided information on in-house research not published in the open literature or not quite ready for publication. There is some work underway at individual mills, at research laboratories of the companies, and by equipment manufacturers which is proprietary in nature and thus cannot be reported here.

The format selected for presentation was that of an annotated bibliography insofar as possible. Eight major categories were selected for presentation of the abstracts including emission control technology, cost and effectiveness of emission control, sampling and analytical techniques, control equipment development, process changes affecting emissions, chemistry of pollutant formation or interactions, new pulping processes, and control systems development. Of course, there is some overlapping of the categories and assignment of abstracts to some categories had to be arbitrary. Within each major category the abstracts are arranged in sub-categories by year of publication.

10.2 EMISSION CONTROL TECHNOLOGY

10.2.1 RECOVERY BOILER SYSTEMS

The recovery furnace and auxiliary equipment such as the direct contact evaporator have long been identified as the major contributors to atmospheric emissions of both particulates and odorous gases. Electrostatic precipitators or scrubbers, or a combination of the two have been used to reduce emissions.

For sometime it has been known that the firing rate of furnaces, above an optimum level, have a direct influence on hydrogen sulfide emissions from the furnace. It has not been until recent years, however, that research has revealed the effect of various operating and process variables on emissions from the recovery boiler system. The most recent research reported as of the end of 1969, has been very enlightening but has barely scratched the surface of the problem. To meet the objective of reduced emissions with modifications to existing systems a more complete understanding is required.

Arhippainen, B., and Westerberg, E. N., RECOVERY FURNACES AND THEIR OPERATION, in Atmospheric Emissions from Sulfate Pulping (E. R. Hendrickson, Ed.), April 1966.

A review is presented of the recovery boiler operations in the sulfate pulping process. The situation can be summarized as follows: (1) significant odor release. (2) Where the black liquor is such that it is difficult to obtain high enough dry solids concentration from a steam evaporator, or where economics are grossly in favor of direct contact evaporation, efficient black liquor oxidation would be necessary to limit odor emission. (3) Electrostatic precipitators can be designed and operated to remove particulate matter almost as efficiently as one wishes. (4) Wet scrubbers, if installed for heat recovery afford some additional dust removal, but will require excessive caustic addition for efficient removal of odorous gases. The role of the recovery boiler in the economics of sulfate pulping is briefly discussed.

Gladding, James N., RECOVERY BOILER CONTROL, TAPPI 49 (5), 112A, (May, 1966).

In the last 30 years developments in both the boiler and instrument industries have permitted the evolution of the recovery system from all that was entirely oriented to the chemical process through manufacture of steam as a by-product to the present time when both steam generation and recovery of chemicals can be done efficiently. At the present time multiple units are being controlled in a central control room with the instrumentation, as far as combustion control is concerned, approximating that of modern power boilers. The efficiencies of the liquor systems have been increased by the development of instrumentations which will more precisely control the density of the liquors entering and leaving the boiler plant. Accidents in recent years have pointed up the necessity for additional safety controls on the auxiliary fuel systems, for control systems on the liquor evaporation, and for established systems for emergency shutdown of the boilers.

Reiche, H., COMBUSTION OF SULFATE BLACK LIQUORS, Papier 21 (10), 593-7, (October 1967), and Papier 21 (11), 834-7, (November 1967).

A boiler manufacturer reports on the operation of soda recovery furnaces, based on techniques currently in use. Initially he discusses furnace construction and the properties that influence the burning of kraft black liquors. The most advantageous combinations of operating variables are described, incl. factors such as the flow of concentrated black liquors through existing conduits and orifices, pressures and temps. required in spraying thickened liquors, size of droplets entering the furnace, temp. ranges within the furnace, the draft required, and means used for introducing fresh air. Based on these factors, the author deals with conditions that could lead to a smoother furnace operation. Tabulated data include the prods. obtained and the conditions required in burning black liquors from straw, wood, and bamboo kraft cooks.

Byers, R. E., COMBUSTION AIR FLOW - ITS MEASUREMENT AND CONTROL, TAPPI 50 (4), 52-8A, (April 1967).

Investments in new boilers and auxiliary equipment show a poor return if they do not perform as an integrated unit, and frequently poor performance is synonymous with unreliable air flow measurement. Equally common is the conversion of a unit for multifuels which has intricate operating procedures and unsafe fuel-air ratios. Few plants escape the symptoms and complications of inaccurate air flow, indicating that the importance of this measurement is not appreciated, nor has the responsibility been clearly defined. There is no perfect primary air flow elt. or universally accepted location, and the configurations of ducts and dampers may not be conducive to a good installation; the degree of acceptance of such an air flow measurement is directly related to who is paying the bill for field research to reinvent solutions to a repetitive problem.

Puhakka, L., SPECIAL CONSIDERATIONS IN KRAFT RECOVERY BOILER DESIGN, Paperi Puu 49 (12), 795-800, (December 1967).

The main functions of kraft recovery boilers are the generation of steam and the regeneration of valuable chemicals. Recovery units resemble conventional steam boilers, but require special features owing to the particular fuel used (black liquor) and the continuous accumulations on the superheater, boiler bank, and economizer tubes, since such deposits will ultimately cause shutdowns. In boiler design, special attention must be paid to wide passages for flue gases; thermal efficiency is of secondary importance. The most sensitive heating surfaces are located outside the boiler, and the boiler itself should be as simple as possible. Hints for the construction of various parts of the recovery unit are given.

Osborne, M. J., SUMMARY REPORT ON ACTIVITIES OF THE BLACK LIQUOR RECOVERY BOILER ADVISORY COMMITTEE, TAPPI 52 (6), 1143, (June 1969).

The gradually evolving by-product utilization development of the pulp and paper industry has been urged forward by the growing concern for water and air pollution. Producers of essentially all types of pulp are interested in the abatement of these pollutions and, if possible, in converting waste effluents into revenue-producing by-products. A number of successful operations are described. Fundamental and practical research is continuing. Technology of by-product production is necessary, but, for successful commercial operation, this technology may be subordinate to such factors as needs of outside industry, changing national and international economies, changing consumer requirements, tariffs, subsidies, political pressures, production costs relative to those of other processes, and the like.

Vegeby, Anders, SCANDINAVIAN PRACTICES IN THE DESIGN AND OPERATION OF RECOVERY BOILERS, TAPPI 49 (7), 103A, (July 1966).

The main differences between the Scandinavian recovery boiler design and operation as compared to the Canadian and American methods are that more of the heat from the combustion of the black liquor is recovered as steam by using economizers cooling the flue gases to about 260°F. The rating of the recovery boiler capacity is much more conservative in Scandinavia than in the United States and Canada to meet the normal increase in pulp mill capacity which will normally be reached by small marginal investments in the pulp mill but which are impossible in the recovery boiler department. At least in Sweden, no direct contact type evaporators are used. To get satisfactory operation for the economizer, hot precipitators, placed between the boiler and the economizer, are used. In Sweden, the black liquor concentration from the evaporation is between 60 and 65%. The differences in investments and operation costs for the Scandinavian and the American and Canadian methods have been calculated. The Scandinavian methods show a gross profit of 29-33%.

Anon., KRAFT RECOVERY BOILER FACES NEW CHALLENGE, Can. Chem. Process. 51 (12), 54-6, (December 1967).

A fluidized bed reactor linked to a conventional kraft liquor recovery boiler can reduce the load on the recovery boiler. This reduction in load is possible because the evaporator is able to burn black liquor at solids contents near 30# (as opposed to the 60% solids required by the recovery boiler). Work is underway aimed at replacing the black liquor recovery boiler with a fluidized bed reactor.

Tirado, A. A., RECOVERY UNITS FOR PULP MILLS UNDER 15 T./DAY, Pulp Paper 42 (23), 26-8, (June 3, 1968).

The design and performance characteristics of kraft black liquor heat and chemical recovery units are described which are particularly designed for use in small mills such as those found in devg. countries. Called RLP units, they include a direct contact evaporator and a 2-stage combustion furnace and feature a low capital investment.

Thoen, G. N., DeHaas, G. G., Tallent, R. G., Davis, A. S., EFFECT OF COMBUSTION VARIABLES ON RELEASE OF ODOROUS COMPOUNDS FROM KRAFT RECOVERY FURNACE, TAPPI 51 (8), 329-33, (August 1968).

The concentrations of odorous compounds in normal kraft recovery furnace stack gas before and after the direct-contact flue gas evaporators were determined under various operating conditions. Results of this testing program indicated that odorous S compounds can be decreased to negligible concentrations if sufficient excess oxygen is available and good turbulence is obtained in the upper oxidation zone of the furnace. Black liquor oxidation has no significant effect on the amounts of odorous material leaving the furnace, but the fineness of the black liquor spray does significantly affect the concentrations of sulfur dioxide and hydrogen sulfide.

Belevitskii, A. M., PURIFICATION OF KRAFT MILL GASEOUS EFFLUENTS IN FINLAND, Bumazh. Prom. 3, 29-32, (march 1965).

In this report from a visit of a Russian delegation to several modern Finn kraft mills, the author discusses the methods used in Finland for the purification of gaseous wastes, and the attitude of the Finn pulp industry toward the problem of air pollution. In all Finn purification installations, emphasis is placed on the recovery of solid particles as a valuable industrial material, and on the recovery of heat from the gases. Air pollution is regarded as a secondary, less important problem. The Finn technical people differ in their opinion as to the way to achieve chemical and heat recovery, and in the 6 mills visited by the delegation, different methods and equipment are used for this purpose. The purification of gases is done in one, two, or three stages, but all installations have a common characteristic, i.e., the use of electrofilters (which are operated automatically). Because of the strict control of the soda recovery furnace variables, these filters operate under standard and constant conditions, and achieve a high purification efficiency. According to Finn specialists, the "hot" electrofilters are more efficient, but they are more difficult to operate and control, and for this reason "warm" filters are used more frequently. Scrubbers are the second important component of Finn purification installations. They are installed either ahead of the electrofilters, or constitute one of the last elements of the system. The main role of the scrubbers is the utilization of heat of the hot gases (a description is given of the design and operation of several scrubbers). The "tail" scrubbers also absorb the foul-smelling S compounds, although no data are available as to their deodorizing efficiency. There are no regulations in Finland concerning the control of air pollution. Consequently, Finn mills have no special installations for the removal of foul-smelling compounds from gaseous effluents of the digester and black liquor evaporation rooms. The efforts are concentracted on the prevention of water pollution.

Dyck, A. W. J., IS YOUR ELECTROSTATIC PRECIPITATOR OPERATING AT MAXIMUM EFFICIENCY?, Am. Paper Ind. 48 (1), 63-4, January 1966).

Methods and applications used in 2- and 3-dimensional model studies of electrostatic precipitators used in air pollution control are briefly examined. The studies concern the determination of optimum design of a precipitator for a specific mill installation with respect to uniform gas flow and maximum operating efficiency.

Lund, H. F., Air Pollution Criteria for Industrial Plant Equipment, U. S. Public Health Service Publication No. 1649, 1966 (pages 207-13).

Economic and technical aspects of plant equipment for pollution control are reviewed. Special attention is directed at high efficiency scrubbers and electrostatic precipitators. Pollution control costs for the various industries most affected are considered.

Blosser, R. O., Cooper, H. B. H., Jr., TRENDS IN REDUCTION OF SUSPENDED SOLIDS IN KRAFT MILL STACK, Paper Trade Journal 151 (11), 46-51, (March 13, 1967).

A survey of secondary wet scrubbing practices in kraft mill air pollution control systems showed that relatively low pressure drop devices may produce a 50-80% reduction in particulate emission from the primary precipitators. The percent reduction is somewhat less when these devices are employed behind Venturi recovery units. Removal efficiency was independent of the type of scrubber used over the range of inlet loadings observed. Final effluent quality was related directly to scrubber inlet grain loading. While effective scrubbing can reduce particulate fallout in the area around a mill, it may also reduce the height of plume rise. Hence dispersion is reduced and an odor problem may be accentuated. It is difficult to predict that any real benefit in either fallout or total emission is obtained with secondary scrubbing behind some of the new precipitators which are capable of 96 to 99% particulate removal efficiency. 6 ref.

Blosser, R. O., Cooper, H. B. H., Jr., PARTICULATE MATTER REDUCTION TRENDS IN THE KRAFT PULP INDUSTRY, Pulp Paper Mag. Can. 69 (3), 55-61, (T77-88), (February 2, 1968).

Recent surveys indicate a trend to reducing particle emissions in kraft mills by installing high-efficiency venturi scrubbers on lime kilns and electrostatic precipitators with rated efficiencies exceeding 97.5% on recovery furnaces. A recent field study of low-pressure-drop secondary scrubbers installed behind primary recovery devices on kraft furnaces showed them to achieve particle-collection efficiencies of 50-80%. Although secondary scrubbers reduce particle emission and fallout in the vicinity of mills, they may also significantly reduce the height of plume rise. 6 ref.

Mita, A., COMPLETE TREATMENT OF PULP WASTE LIQUOR AND UTILIZATION OF BY PRODUCTS, Kami-pa Gikyoshi 22 (10), 515-32, (1968).

When black liquor was first baked and then burned in an oxidizing atmosphere, the resultant ashes (I) contained 80.7% Na_2CO_3 and 17.1% Na_2SO_4, but neither $Na_2S_2O_3$ nor Na_2S. The ashes (II) obtained in a similar manner from the spent liquor of the neutral sulfite semichemical (NSSC) process contained 59.6% Na_2CO_3 and 32.3% Na_2SO_4. Sulfitation of I made it possible to reuse I for NSSC and Na-base acid sulfite cooking liquor. Carbonization of an aqueous solution of II in NH_3 converted both Na_2SO_4 and Na_2CO_3 to $NaHCO_3$, which was recovered from the mother liquor containing $(NH_4)_2SO_4$. The NSSC spent liquor was subjected to evaporation and combustion to yield an aerosol containing Na. Air oxidation of this aerosol together with SO_2 gave anhydrous Na_2SO_4 powder of 95-8% purity. It is proposed to use H_2S liberated from the petroleum refining process as a kraft cooking liquor together with NaOH.

Jones, K. H., Thomas, J. F., Brink, D. L., CONTROL OF MALODORS FROM KRAFT RECOVERY OPERATIONS BY PYROLYSIS, J. APCA 19 (7), 501, (July 1969).

The major source of malodorous emissions which emanate from kraft mills is the recovery furnace and its associated direct contact evaporator. The primary reasons for this problem are gross furnace overloading and/or inadequate design. Existing recovery furnaces are incapable of carrying out, to an acceptable degree of completion, the complex sequence of physical and chemical steps which describe combustion. These steps are evaporation, sublimination, pyrolysis, recombination, and oxidation. A simplified odor model is presented which establishes the constraints which must be placed on the combustion phase of the recovery operation if environmental concentrations of malodorous compounds are to be held below their respective threshold odor levels. The pyrolysis and recombination steps of combustion have been isolated for study because they encompass the reaction mechanisms responsible for malodorous compound production. The findings of the steady state pyrolysis study indicate that the optimization of pyrolysis appears to be a very desirable process technique for abating malodorous emissions from kraft mills. The comprehensive data obtained in the study has engendered the current design and construction efforts toward a pilot plant operation.

10.2.2 BLACK LIQUOR OXIDATION

Nearly all of the emission of H_2S from the direct contact evaporator and much of that from the multiple effect evaporators can be traced directly to the presence of Na_2S in the black liquor. Work done in the late 1930's demonstrated that oxidation of the sulfide to thiosulfate reduced the chances of H_2S formation appreciably. Much work has been done on black liquor oxidation since that time. Numerous BLO systems have been developed to meet specific problems. As of late 1969, however, gaps in our knowledge still existed. Problems of understanding the mechanisms of oxidation, foaming, economics, and reversion are some of those still remaining to be solved. Since BLO will probably continue to be of importance as a means of odor reduction for some time to come, these gaps need to be filled.

Hendrickson, E. R., and Harding, C. I., BLACK LIQUOR OXIDATION AS A METHOD FOR REDUCING AIR POLLUTION FROM SULFATE PULPING, J. APCA 14 (12), 487-90, (December 1964).

The sources of odorous air pollutants from kraft pulping operations are discussed. One of the major sources is improper operation of the recovery furnace. Odors from this source can be reduced considerably by oxidation of the black liquor prior to evaporation and burning. This procedure has been used with considerable success in the NE and NW sections of the U. S. However, kraft pulp production in areas where southern pine is the basic raw material results in a high degree of foaminess of the black liquor making the above procedure impractical. Various attempts to oxidize black liquor resulting from the pulping of southern pine have met with only limited success. Various procedures for oxidizing black liquor are discussed and the results of stack sampling in U. S. pulp mills with and without an oxidation unit are presented. 19 ref.

Murray, F. E., CONTROL OF ODOR IN KRAFT PULPING, World Paper Trade Rev. 162 (11), 802, 804, (September 10, 1964).

The source of odor at a kraft mill (sources are illustrated by chemical reactions describing the preparation of cooking liquor from Na sulfate and the cooking and recovery cycles) are discussed, and possible measures (e.g., oxidation of black liquor) to control or eliminate kraft pulping odors are outlined briefly.

Murray, F. E., THE OXIDATION OF KRAFT BLACK LIQUOR, in Atmospheric Emissions from Sulfate Pulping (E. R. Hendrickson, Ed.), April 1966.

A review is presented of kraft black liquor oxidation systems. Included are discussions of the theoretical mechanisms, catalysts, and the kinetics of the reactions. The sources which might be affected by the process of BLO are described. Descriptions are presented of the various types of oxidation systems used for both weak and concentrated liquor. An economic analysis and citation of research needs complete the discussion.

Alferova, L. A., and Titova, G. A., OXIDATION OF SODIUM SULFIDE AND MERCAPTIDE IN BLACK LIQUOR, Bumazh. Prom. (10), 5-6, (October 1966).

The recommended method for deodorization of foul-smelling kraft mill effluents is a two-stage oxidation, first by aeration, then by chlorination. The spent air from the first stage is purified jointly with the gaseous wastes. However, if oxidation is carried out so as to convert the sulfides and mercaptides to sulfates and sulfonic acids, respectively, the formation of foul-smelling compounds and their evoln. can be prevented. To determine the best conditions for such oxidation, aqueous solutions of hydrogen sulfide, methyl mercaptan, and of their Na salts, were oxidized by aeration at various air flow rates, various temps., and within a wide range of pH. For all solutions, the rate of oxidation was determined mainly by temperature and the surface area of contact between the solution and the oxidizing agent. Both the hydrogen and the hydroxide ions had a catalytic action, and the course of the reaction, as well as the end products were determined by the pH. To achieve a large contact area, aeration should be done in an app. of the atomizing type. The recommended conditions are a temperature of 80-100°C., and a pressure of 4-6kg/cm.^{2}. Under these conditions, the reaction is of the zero order, and its rate is determined by the ionic strength of the black liquor and its pH. The final pH must not be lower than 12.6, as at a lower pH other oxidation products (thiosulfates, sulfites, polythionates, etc.), predominate. Also at a pH below 11, MeSH is partially converted to methyl and hydroxide sulfide, the latter escaping from the solution. The oxygen consumption for oxidation under optimum conditions is approximately equal to the theoret. calcd.

Owens, V. P., TRENDS IN ODOR ABATEMENT FROM KRAFT MILL RECOVERY UNITS, Paper Trade J. 152 (33), 52-4, (August 12, 1968).

New developments in odor abatement in kraft mill chemical recovery units are discussed, including direct-contact evaporation of the black liquors using clean air rather than flue gases, elimination of direct-contact evaporation from the recovery cycle, and the use of a black liquor oxidation stage prior to direct-contact evaporation. 7 ref.

Zerebeski, O. H., HOW KAMLOOPS [PULP & PAPER CO. LTD., KAM-LOOPS, B. C.] STOPPED "M[Ill] O[Dor]", Pulp Paper 42 (25), 40-3, (June 17, 1968).
The weak black liquor oxidation system at the mill is described. Basically, the system consists of a reactor tank continuously fed with weak black liquor. Low pressure compressed air is injected into the bottom of the reactor through a dispersing ring, causing the formation of foam which rises to the top. A mech. foam breaker separates the gaseous and liquid phases. The gases are discharged to the atmosphere through roof vents. Oxidized liquor is drawn off from the bottom of the reactor. Startup problems were experienced and the system had to be enlarged before a satisfactory oxidation efficiency of 95% was attained (weak black liquor sulfide loading below 8.0 g/liter) installation of a stilling tank following the reactor tank eliminated pumping problems with the oxidized liquor.

Laasonen, E., EXPERIENCE WITH BLACK LIQUOR OXIDATION AND ODOR CONTROL AT THE KUUSANNIEMI SULFATE MILL [OF KYMIN OY.], Paperi Puu 49 (4a), 217-19, 221-6.

A review of pertinent research work reported in the literature is followed by a report on the R & D work done at this Finn kraft mill, supplemented by 2.5 years of operating experience with the liquor oxidation system. By means of special measures, both odor and corrosion problems have been largely eliminated at the mill. 10 ref.

Menzies, M. A., OXIDATION OF PINUS RADIATA KRAFT WEAK BLACK LIQUOR, Appita 22 (1), 16-24 (July, 1968).

Oxidation studies on weak black liquors have shown certain advantages due to S stabilization and reduction of odor. However, the practical oxidation of black liquor has not found wide acceptance because of difficulties caused by excessive foam formation. A study was made of the oxidation of Pinus radiata kraft weak black liquor using a falling-film type of contacting system. The liquor descends over the face of a vertical sheet of packing cocurrently with a stream of air. Recirculation of the liquor allows the simulation of an oxidation tower having the height required on a mill scale. Excessive foam formation was not experienced with the unit used when oxidation rates were up to 4 lbs. Na sulfide/hr. over a packing surface of 100 sq. ft. Effect of gas velocity, liquor flow rate, sulfide concentration, and the configuration of the packing surface were studied, and a mathematical model of the oxidation process was developed based on the 2 film resistance theory of absorption. This model was appl. in the design of a mill scale unit. The factors that require consideration for designing an economical pract. system are discussed. Publ. data of the oxidation reactions are also considered in relation to the results obtained in this study. The layout of the lab. app. and details of the packing strips are depicted, and symbols used by the author are given in a glossary. 12 ref.

Kacafirek, Stanislav, Kubes, Jiri, Racek, and Vaclav, PRACTICAL EXPERIENCE WITH OXIDATION OF BLACK LIQUOR IN THE STETI PULP MILL, Papir Celul 23 (7), 194-6, (1968).

The main systems for the oxidation of black liquor are mentioned and the equipment installed in the cited pulp mill by BT-Metoder Stockholm is described. It consists of 2 oxidation towers with 3 perforated plates through which air is passed countercurrently. The foam is passed into a storage tank equipped with a device for mech. breaking of the foam. The height of the pipe from the foam layer on the top of each tower to the tank is 1700 mm., which was found to be optimal. At present, the equipment operated with a load of 3.3 tons of liquor/$m.^2$/hr. The air-liquor ratio is 1:60-5 for liquor contg. 16% dry matter; this concentration is advantageous because the sepn. of sulfate soap does not take place. The course of chemical reactions during oxidation of black liquor and their importance for the reduction of losses of S and limiting of equipment corrosion is discussed. Analytical results characterizing the operation of the equipment as well as those of corrosion tests of oxidized and nonoxidized liquors performed by detn. of wt. losses of steel samples and by polarization measurements are also given.

Galeano, S. F. and Amsden, C., WEAK BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN, Paper presented at the 62nd Annual Meeting of APCA, New York, June 1969.

Oxidation of black liquor (BLO) is one of the most effective ways to control odor from the operation of kraft pulp mills. Maximum reduction in atmospheric emissions is obtained when the weak black liquor is oxidized. Up until this time, the foaming properties of weak black liquor from pulping southern pine have hindered the development of successful oxidation schemes for weak liquor.

The possibility of using molecular oxidation as a means of oxidizing weak black liquor in a pipeline was set forth some ten years ago. Economic considerations weigh heavily, however, in the use of pure oxygen. The decrease in costs of tonnage oxygen has been dramatic over the past few years. Also, the possibility of new markets for tonnage oxygen in waste treatment systems could further enhance the economic balance over using the gas.

An advantageous market condition for a pipeline supply of oxygen to the new kraft mill of Owens-Illinois at Orange, Texas, made a study of a pure oxygen system appealing. A complete trial was planned in which all of the effects (BLO) in the system could be evaluated. The paper describes the system tested at the Orange mill in which all of the weak kraft black liquor was successfully oxidized in a tubular reactor at production levels ranging from 700 to 1,000 tons of air dried pulp per day. For this installation, it was estimated that the breakeven point in comparing the system with a conventional system would occur where oxygen costs were below $8.50 per ton. The trial was conducted during October and November, 1968.

Obviously, the design and installation of air oxidation units is mainly a problem to be solved for each individual mill. The implementation of a tonnage oxygen system is likewise an individual mill decision and will depend largely on the price and availability of oxygen.

Martin, F. R., IMPROVED ODOR CONTROL THROUGH SECONDARY OXIDATION OF KRAFT BLACK LIQUOR, Pulp and Paper 43, (June 1969).

Oxidation of kraft black liquor is an industry accepted method for preventing the evolution of H_2S during direct contact evaporation by recovery furnace flue gas. This paper reports that H_2S evolution may occur in spite of complete weak black liquor oxidation. During studies of H_2S emissions from direct contact evaporators, reversion of oxidized liquor in multiple effect evaporators became apparent. A secondary oxidation step which results in improved odor control is described.

Shah, I. S. and Stephenson, Wayne D., WEAK BLACK LIQUOR OXIDATION SYSTEM: ITS OPERATION AND PERFORMANCE, TAPPI 51 (9), 87A, (September 1968).

After a thorough analysis of the advantages of weak and strong black liquor oxidation and after an evaluation of weak black liquor oxidation in a pilot plant (capable of handling 100 gal/min of liquor equivalent to 50 tons/day of pulp production), a full-scale weak black liquor oxidation system was installed. The system is designed to handle 400 gal/min of weak black liquor at 16-17% solids concentration and 4.0-6.0 g/liter of sodium sulfide content. The wood furnish is a mixture of pine and hardwood, with pine content varying to a maximum of 60%. The commercial system has successfully operated since startup and provides essentially 100% oxidation efficiency, even with variations in liquor flow and sodium sulfide content from 300 to 475 gal/min and 2.3 to 6.6 g/liter, respectively. The total operating power, including fan, pump, and foam breakers is less than 100 hp. The extensive and stable foam that is formed during oxidation is efficiently handled and causes no operating problems. As a result of the oxidation of weak black liquor, the sulfidities of green and white liquors are raised from 18.2 to 27.1% and 22.6 to 27.9%, respectively. The total lime requirement is reduced by 0.085 lb of lime per gal/min of green liquor, a 15.4% reduction. The amount of hydrogen sulfide leaving the recovery furnace stack is reduced by 98.5%. The biochemical oxygen demand of the multiple effect evaporator condensate is reduced by 27% and the pH raised from 6.5 to 9.0, thus making the 175 gal/min of the evaporator condensate suitable for reuse in the pulp mill. Overall, a significant reduction in odor and chemical loss is achieved, as a direct result of the weak black liquor oxidation system.

10.2.3 MULTIPLE EFFECT EVAPORATORS

The multiple effect evaporators are usually classified as a low volume, high intensity source of odors in a kraft mill. Emissions from this source are variable. Operating and process variables which affect emissions are largely unknown, but BLO may result in a reduction of some of the odorous sulfur compounds. In some of the newer recovery system designs, the direct contact evaporator is eliminated and the black liquor is evaporated to high solids content in the multiple effect evaporators. Operational problems may result. Means for maintaining the high evaporation rate and a better understanding of the effects of operating and process variables on emissions need to be investigated further.

Droy, M., MODERN METHOD OF CONCENTRATING BLACK LIQUORS, Papier Carton Cellulose 17 (2), 77-80 (March/April 1968).

A newly developed multiple effect evaporator for the concentration of black liquors is described which employs a combination "upflow-downflow" system. The upflow tubes merely serve to facilitate the diffusion of the liquor in the downflow tubes. This obviates the need for circulation pump at each stage. A special reheater is used to heat the liquor between successive stages. The new system features circuit simplicity, ease of maintenance, rapid startup, and a minimum control equipment requirement.

Arhippainen, B., Jungerstam, B., OPERATING EXPERIENCE OF BLACK LIQUOR EVAPORATION TO HIGH DRY SOLIDS CONTENT, TAPPI 52 (6), 1095 (June 1969).

Operating practice in most modern Scandinavian kraft mills includes evaporation of the black liquor to 60-65% dry solids content in multistage evaporators and direct firing of the strong liquor. In most cases, the selection of this system in preference to a direct-contact evaporator system can be justified by economical consideration alone, with no regard to air pollution. Operating experience with multistage evaporation plants operating at high dry solids content is reported. The heat transfer characteristics of black liquors are related to reported physical properties, and the importance of increasing boiling point rise with increasing dry solids content is pointed out. The scaling properties of black liquors at high dry solids content is related to their chemical properties. The importance of maintaining a low temperature in the high dry solids effect, a reasonable content of residual alkali, and low contents of sodium sulfate, carbonate, and fiber in the black liquor, efficient soap separation, and high white liquor clarity, in order to limit scaling, is stressed. It is indicated that the optimum product dry solids content may be higher than the 62-63% presently achieved with natural circulation evaporators, because of favorable secondary effects in the recovery boiler. Some Scandinavian mills use forced circulation in the high dry solids effect, whereby 65-67% dry solids content can be reached. The use of forced circulation in the high dry solids effect is not always justifiable in Scandinavia, but it is assumed that forced circulation should be a first choice in many areas with lower power costs.

Stacie, J. H., Wilhelmsen, L. A., MAINTAINING MULTIPLE EFFECT EVAPORATION RATE, TAPPI 52 (7), 1278, (July 1969).

A material containing polymethacrylate as the active ingredient was added to kraft black liquor feed to multiple effect evaporators at various rates, in an attempt to reduce tube scaling and prevent loss of heat transfer. Although there is substantial evidence that this material reduces the rate of scale formation, the evaluation is clouded by the usual operating variations encountered in black liquor evaporation. An increase in overall evaporation capacity was found when this material was added continuously in conjunction with scheduled water boil-outs and good maintenance of the associated equipment.

Morrison, J. L., COLLECTION AND COMBUSTION OF NONCONDENSIBLE DIGESTER AND EVAPORATOR GASES, TAPPI 52 (12), 2300-, (December 1969).

Vaporspheres have successfully contained the odorous, noncondensible organic vapors from both batch and continuous digesters and from black liquor evaporators. The vaporsphere systems not only reduce the local mill odor emission but also reduce the fuel requirements of the lime kiln in which the gases are burned. A vaporsphere, or gas accumulator, is a 27-ft. steel sphere with a lightweight-fabric diaphragm attached inside around the equator of the sphere. Gases enter through the bottom of the vaporshpere and are retained under the diaphragm which "floats" up and down on the gas cushion. As the vaporsphere fills, an automatic valve discharges just enough gas to equal the net flow generated for each cooking cycle. The gases leaving the vaporsphere are then passed through a scrubber.

10.2.4 LIME KILNS

Particulate losses from lime kilns represent a direct loss of a valuable chemical and thus have stimulated considerable research and development activity for emissions control. Little is known, however, about the lime kiln as a source of odors and SO_2. The origin of the odorous gases reported by some investigators has not been satisfactorily demonstrated. Many workers report no emission of SO_2 even when noncondensibles are being burned in the kiln. This phenomenon also has not been explained adequately. Fluidized bed calciners as substitutes for kilns have not been adequately evaluated with respect to emissions and no information appears to be available regarding the use of such systems for destroying noncondensibles.

Taylor, C. E., LIME KILNS AND THEIR OPERATION, in Atmospheric Emissions from Sulfate Pulping (E. R. Hendrickson, Ed.), April 1969.

The lime kilns of the kraft pulping industry constitute an integral part of the causticizing and chemical recovery processes. The application of emission control systems to the kiln has been typified by evolutionary changes. The current systems in use are: impingement scrubbers and higher energy venturi scrubbers. A description of a typical impingement scrubber installation is given, followed by operational and cost data applicable for a kiln serving a pulp mill of about 300 tons/day capacity. Several factors influence the scrubber system operation. Technically, from an air quality control point of view, this scrubber system does a very adequate job when operated properly. However from an operator's view, these scrubbers have some limitations and disadvantages, specifically the deposition of calcium resulting in plugged screen plates, and the problem of water balance. A typical venturi scrubber system is described; operational and cost data are presented. Reports indicate very low maintenance for this equipment with minimum attention from the operator. The quantity of odor constituents emitted from lime kilns is generally small in comparison with other sources in the pulp mills. As improvements are made in over-all odor control, the factors influencing odor emission from the kilns will have to be thoroughly evaluated in order to minimize their formation and release. Possible sources of sulfur compounds for the kilns system are considered. Conclusions drawn from survey work in kiln odor control are presented. The best method of assuring minimum odor release appears to be a combination of low sulfur fuel, good combustion control, and adequately washed lime mud. Recent developments with the fluidized bed calciner as a substitute for the kiln are discussed. Research and development needs for control in this area are listed.

10.2.5 MISCELLANEOUS RESEARCH

Amarinei, E., Weiss, E., Brasat, R., DEODORIZATION TRIALS FOR KRAFT FLUE GASES, Celuloza Hirtie,15 (1) 23-9 (January 1966).

Laboratory and pilot-plant trials with kraft process-derived gaseous effluents are reported. Both the flue gases and the black liquor itself were oxidized, and the gases were tried successively with solutions of Ca hypochlorite and NaOH. Each step resulted in a reduction of odiferous noxious components. Results indicated that the process is applicable on an ind. scale and could remove more than 95% of the volatile S compounds. 21 refs.

Alferova, L.A., Panova, V.A., and Titova, G.A.
DEODORIZATION OF EFFLUENTS FROM THE MANUFACTURE
OF KRAFT PULP, Bumzah, Prom.38 (6) 5-8 (June 1963).

Analyses of black liquor evapn. effluents and of digester relief condensate led to the conclusion that the deodorization of these two effluents should be carried out separately, because of the different cpn. of the S compounds. The odor of the evapn. effluents which contain mainly H_2S, and MeSH can be controlled by chlorination or by aeration and chlorination. On the other hand, the condensates usually contain also Me_2S, Me_2S_2, and small amounts of other S compounds., and their deodorization by extn. or distn. presents the possibility of recovering some of the S compounds. Digester relief condensates from continuous cooks contain more MeSH than H_2S, and little or no turpentine (in such cooks, the bulk of turpentine remains in the black liquor). Experimental data presented show that the S compounds can be removed from the condensates by extn. with sulfate turpentine. For example, a condensate originally containing 52 mg. Me_2S and 11 mg Me_2S_2/liter, contained no S compounds flg. three extns. with turpentine. Equally good results were obtained by fractional distillation. Complete deodorization of the black liquor evapn. effluents was obtained by aeration in a packed tower at an air consumption of 2 cu.m./ 1 cu.m. effluent, fld. by the removal of residual odor by chlorination, at a Cl consumption of 0.7 - 8 kg./t. pulp produced. The deodorized effluent contained 0.7 mg Cl/liter. Diagrams are given of installations for the two-stage purification of evapn. effluents, and for the extn. and distn. deodorization of relief condensates.

Wulfinghoff, M. Disposal of Process Wastes - Liquids, Solids, Gases, Chemical Publishing Co., New York, 1968 (240 pages).

The 18 separate contributions to this symposium dealt with industry's contributions toward maintaining a clean environment, developments in chemical effluent reclamation, waste treatment in the chemical industry, ion exchange as a unit operation in treatment of industrial waste waters, removal and recovery of proteins. IR spectroscopic detn. and removal of oil contaminants (emulsions) from waste waters, biodegradable detergents, reclamation of radioactive waste water, encapsulation of nuclear wastes, air pollution and its control, treatment of waste air and gases in the process inds., catalytic afterburning of industrial waste gases, the Bayer double-contact process for sulfur dioxide conversion into trioxide, chem. eng. methods for removing inorganic emissions, removal of industrial wastes by incineration, ion-exchange and extn. methods in the rare metal inds., and a report on progress made during 1964 - 1966 in industrial waste treatment. A selected bibliography, a glossary of terms, conversion tables, and a subject index are appended.

Shah, I. [KRAFT] PULP PLANT POLLUTION CONTROL, Chemical Engineering Progress 64, (9) 66-77 (Sept., 1968).

A detailed description is given of the kraft pulping process, and the steps which are being taken in each stage of the process to eliminate the emission of contaminants, such as hydrogen sulfide, mercaptans, or methyl sulfides, to the atmosphere or to waste waters. 17 ref.

Roberts, D. PRINCE GEORGE PULP & PAPER LTD. ACHIEVES PRODUCTION TARGET; ODOR AND EFFLUENT CONTROL ARE MAJOR CONCERNS; PROCESS AND EQUIPMENT DETAILS, Pulp and Paper Magazine, Canada 67 (10) 75-88 (Oct. 1966).

A detailed illustrated description is given of the new $84 million kraft mill of Prince George Pulp & Paper Ltd. in the interior of B.C., which has a pulp capacity of 360 and a bag paper and linerboard capacity of 300 daily t. A process flow chart is included. Highlighted are the extensive installations for odor control (a Trobeck-Ahlen oxidation and Lundberg-Ahlen vapor-treatment system utilizing bleach plant effluent for gas cleaning) and for effluent treatment (save-all filter, centrifugal dewatering, soapy froth skimmer, aeration lagoons, etc.).

Pucek, B., CONTROL BY OPTIMIZATION IN THE PULP INDUSTRY, Sb. Vyskum. Prac Odboru Celulozy Papiera (10) 219-28 (1965).

The principles of optimization control, i.e., cases when the relation between the variable controlled and the controlling factor can be represented by a curve with a max.

is discussed in general terms. Such control can be achieved manually or automatically. At the Pulp & Paper Research Institute in Bratislava, a control instrument was developed which can achieve optimization and operates on the basis of a compensating recorder. The control system was applicable to the production of dimethyl sulfide from spent pulping liquors and to the combustion of hydrogen sulfide in the process of spent liquor chemical recovery. The operation of the system is described and its efficiency illustrated by a graph. 6 ref.

Misra, N.D. SODA RECOVERY; THE LIFE-BLOOD OF THE PAPER INDUSTRY, Indian Pulp Paper 22 (12) 679-81 (June, 1968).

The nature of soda losses when blowing the digester and in stacks, in the brown stock washing system, in black liquor evaporators, in thin black liquor, and in heat recovery furnaces and causticizers are all discussed briefly. The vital importance of good soda recovery is emphasized.

Lenz, W., Tirado A.A. MEXICAN KRAFT MILL USES OBSERVERS TO CHECK ITS ODOR CONTROL PROGRAM, Paper Trade Jour. 150 (34) 64, 68 (Aug. 1966).

A program for evaluating the effectiveness of odor control at the kraft pulp mill of Loreto Y Pena Pobre (Mexico City) consists in getting weekly odor reports from 15 to 20 "observers" chosen among people who are not connected otherwise with the mill, who live within a 7 km. radius of the mill, and who in many cases, have frequently complained about the mill's odor.

Landry, Joseph E., and Longwell, Daniel H. ADVANCES IN AIR-POLLUTION CONTROL IN THE PULP AND PAPER INDUSTRY, TAPPI 48 (6), 66-70 (June, 1965).

Considerable progress is being made in the application of existing and the development of new control measures. Equipment available for maintaining air quality in the vicinity of kraft pulp mills, advances in the control of odors and particulates, and some analytical methods used for detecting the efficiency of control measures are summarized. 10 ref.

Institute of Paper Chemistry, PROGRESS IN ALKALINE PULPING (1966), TAPPI 51 (6) 75-87A (June 1968).

This bibliographical survey of the indicated literature reviews advances in the manufacture of alkaline pulps from woody and nonwoody fibers, the complete pulping/recovery cycle (white liquor, black liquor, chemical recovery, and by-products), bleaching of alkaline pulps, new mill constructions, and expansions (modernizations), corrosion problems, and stream and air pollution. 346 ref.

Harding, C. I., Landry, J. E., FUTURE TRENDS IN AIR POLLUTION CONTROL IN THE KRAFT PULPING INDUSTRY, TAPPI 49 (8) 61-7A (August 1966).

The reasons for the mounting pressure on the kraft industry to reduce atmospheric emissions are reviewed. Measured gaseous and particulate emission figures are presented together with recent advances in emission control technology as bases for proposing the types and extent of emission control to be utilized by the pulp industry during the next five years. 1 ref.

Grossmann-Cooper, Anna, Sulfur Oxides and Other Sulfur Compounds: A Bibliography with Abstracts, Public Health Service Publication No. 1093, 1965 (383 pages).

Nearly 1000 annotated references are arranged under 13 subject categories, indexes of authors, titles (separated for each of the 13 subjects), and geographical locations are appended. Emphasis is on sources, effects, and monitoring of air pollution caused by S compounds.

Freyschuss, S., PULP MILL WASTE IN SWEDEN, Pulp Paper Mag. Can. 68 (2), T35-9, (February 1967).

Water and air pollution (Odor) problems of Swedish pulp mills (48 Sulfite, 34 kraft installations) are surveyed, along with control measures taken (sedimentation, basins, sediment treatment, waste water discharge and diln., etc.) and contemplated. Discharges from modern mills are only about 50% of what they were 5 years ago, owing largely to advances in pulp washing methods and equipment and the introduction of continuous pulping processes. Further improvements may be expected in sulfite pulping from the increased use of soluble-base liquors, and in kraft pulping from reduced water consumption. The latter may be held so as low as 75 cu.m/t of unbleached pulp, which is only about 1/3 of the average for present Swedish kraft mills, but the present profitability limit for the rend. of washing losses would seem to be a loss of Na sulfate of about 15 kg./t. of pulp.

Galeano, S. F., REMOVAL AND RECOVERY OF SULFUR DIOXIDE IN THE PULP MILL INDUSTRY, Ph.D. Thesis, University of Florida, 1966 (254 pages).

The technical and economic feasibility of a purification system for the removal and recovery of SO_2 from pulp mill waste gases was studied. An experimental pilot plant consisting of a Venturi scrubber and a cyclone was used. Two different scrubbing solutions were employed: a carbonate solution (simulating a NSSC mill) and weak black liquor (simulating a kraft mill). With the carbonate solution, SO_2 removals in excess of 90% were obtained, the system being both technically and economically sound. With the weak black liquor scrubbing solution, economy becomes a matter of the particular conditions in individual mills.

Galeano, S. F., Adams, F.A., AS DEMAND FOR POLLUTION CONTROL GROWS, SO DOES PROGRAMMING SYSTEM NEEDS, Pulp Paper 42 (28), 21-4 (July 8, 1968).

A program is described for evaluating the present and future pollution level of a mill on the basis of the production level and the implementation of pollution control measures.

Evans, J. C. W., CANADIAN [PULP AND PAPER] INDUSTRY ADVANCES IN AIR AND WATER EFFLUENT CONTROL, Paper Trade Journal 152 (40), 50-60 (September 30, 1968).

Rather detailed summaries are presented of the following papers given at the 4th Paper Industry Air & Stream Improvement Conference held by the Tech. Section, Can. Pulp & Paper Association at Halifax, Nova Scotia: Smith, R.C.: Outside dry barking of hardwoods and softwoods.; Morris, J. V., and McGill, L.H.: Mechanical aerator [for water aeration] testing at London, Ontario.; Hochmuth, F.W.: Odor control system for [kraft] chemical recovery units.; Harvey,E.H., and Devine, T.M.: [effluent] bark fines removal and recovery system.; Parker, G.R., and White, L.C.: Effluent treatment at the Hinton [Alberta] kraft [pulp] mill [of North Western Pulp & Power Ltd.]; Malarkey, E.J., and Rudosky, C.: [Air Pollution control with] high efficiency kraft [pulp] mill [electrostatic] precipitators [incombination with gas scrubbers].; Wong, P.M.: Primary treatment of effluent at Great Lakes Paper Company's kraft mill; Clement, J.L. and Elliott, J.S.: Kraft recovery boiler design for odor control.; Lankenau, H.G. and Flores, A.R.: Multiple effect evaporation of kraft mill black liquor to 55-65% solids.

Canadian Chemical Processing, POLLUTION: CLEANUP IN THE PULP MILLS, Can. Chem. Process. 50 (12), 43-7, 60 (December 1966).

Air and water pollution, already a problem in some Canadian provinces (e.g., British Columbia) is being further aggravated by new or the expansion of present pulp and papermaking facilities. This report summarizes to what extent the Canadian government and the pulp and paper industry are cooperating (e.g., fiscal incentives offered by the government) in an effort to reduce pollution. Some details are given of the types and amounts of pollution produced, together with pollution abatement measures taken by some of the mills.

Banciu, I., DEODORIZATION SYSTEMS USED IN THE KRAFT PULP INDUSTRY, Celuloza Hirtie 17 (1), 36-40 (January 1968).

This is a brief review of some odor control measures employed at various American and European kraft installations, including the principles involved (black liquor oxidation, catalytic oxidation, flue gas combustion in recovery furnaces and lime kilns, and gas scrubbing with various chemicals). 14 ref.

Anderson, K., HOW KRAFT PULP MILLS CAN DECREASE COOKING ODORS, Pulp Paper Intern. 9 (6), 52-3 (June 1967).

Kraft pulp mill odor can be decreased by decreasing the amount of organic sulfur compounds formed during the cook. The influence of various cooking variables on organic sulfur compound formation is outlined. It is shown that organic sulfur compound formation can be reduced by incorporating a Sion-poor or lignin-poor second stage into the cook. The latter case, which involves the withdrawal and cooling of the cooking liquor when the cook reaches the maximum temperature, is the more attractive. Reducing kraft mill odor through oxidation, absorption, and extn. of sulfur compounds in the gaseous emissions from a kraft mill is also discussed along with steam stripping of digester condensates.

Adams, Donald F., A SURVEY OF EUROPEAN KRAFT MILL ODOR REDUCTION SYSTEMS, TAPPI 48 (5), 83-7A (May 1965).

During the spring and summer of 1964, a study was made of selected kraft pulp mill installations in Norway, Sweden, Finland, France, Italy, and Austria. Information was obtained by personal interviews with tech. personnel in the mills and research workers in institutes and universities. Equipment in 18 mills was observed, and the unique features of these installations are reported. The principal methods contributing to odor reduction included incineration, alk. absorption, heat recovery, black liquor oxidation, and Cl treatment. 6 ref.

Harding, C. I. and Galeano, S. F., USING WEAK BLACK LIQUOR FOR SULFUR DIOXIDE REMOVAL AND RECOVERY, TAPPI 51 (10), 48A (October 1968).

Pulp mill air pollution problems are of three basic types: odor, particulate emissions, and sulfur dioxide emissions from power boilers. Black liquor oxidation is the single step most effective for odor reduction. Work has been completed on a pilot scale on the development of a weak black liquor oxidation system using southern kraft liquor with subsequent use of the liquor for SO_2 scrubbing of power plant flue gases. The results of this work show that weak black liquor from southern kraft mills can be oxidized effectively by using kerosene for foam control. The scrubbing of the flue gas with the weak liquor by using a moderate head loss Venturi scrubber (approximately 14 in. H_2O) showed consistent SO_2 removal efficiencies above 92%. Work by earlier investigators was confirmed, showing that approximately 80% sulfide oxidation gave the most effective SO_2 absorption without any measurable release of hydrogen sulfide. Complete oxidation of sulfide enhanced the formation of sulfates which inhibited SO_2 removal during scrubbing. The liquor can be recirculated for multiple passes through the scrubber provided the pH is kept sufficiently high to prevent lignin precipitation. The economics of the system indicate that a net savings of about 30¢/ton a.d. pulp can be effected by installing the integrated oxidation and scrubbing system without any dollar credit for reduction in SO_2 emissions.

Tirado, A. A. and Gonzales, V. P., TEN YEARS EXPERIENCE IN ODOR CONTROL AT THE LORETO Y PENA POBRE KRAFT MILL, TAPPI 52 (5), 853, (May 1969).

Additions and modifications were made to a kraft mill odor control system, which has been operated for 10 years. Emphasis was placed on determining and maintaining proper reaction conditions for each process. Odor levels were monitored at various locations around the mill, and modifications to the odor control system were based on these reports. The original odor index in 1957 was 0.072; and by 1967 the average was 0.00187, a reduction of 97%. The absorption of mercaptans and other sulfur compounds in white liquor, to make a special cooking liquor, was successfully applied. As a result, pulp quality was improved and odor emission dropped about 67%. Lime kiln emissions were controlled by careful operation.

Walther, J. E. and Amberg, H. R., A POSITIVE AIR QUALITY CONTROL PROGRAM AT A NEW KRAFT MILL, Paper to be published J.APCA, (J nuary 1970).

In the design of the Crown Simpson bleached kraft mill at Fairhaven, California, the latest technological developments in odor and dust control were used to design a system capable of removing in excess of 90% of the malodorous sulfur emission and more than 98% of the dust load. The odor control system consists of high efficiency black liquor oxidation, noncondensible gas burning, and stripping of "foul" condensate followed by burning of the off-gases. The dust control system on the recovery furnace consists of a high efficiency electrostatic precipitator followed by wet scrubbers. The lime kiln gases are scrubbed in a Venturi scrubber and the smelt dissolver stack was equipped with demister pads. The gases from the lime kiln, power boiler, recovery furnace, and black liquor oxidizer are combined and discharged through a 310 ft. stack. A complete emission inventory has been conducted and the volume, composition and quantity of materials discharged are presented.

Walther, J. E. and Amberg, H. R., THE STATUS OF ODOR CONTROL IN THE KRAFT PULP INDUSTRY, paper presented at the National Meeting of AIChE, Portland, Oregon, August 24 - 27, 1969.

Technological advances in the control of odor from kraft pulp mills have been rapid and new installations presently discharge only a fraction of the malodorous sulfur compounds discharged by the older mills. Emission surveys conducted at mills which do not have odor control equipment indicate a total reduced sulfur emission rate of about 20 lbs./A.D. ton of pulp can be expected. New mills employing high efficiency oxidation of black liquor and burning of noncondensible gases from the digesters and multiple-effect evaporators can reduce the emission rate to about 1.5 lbs/ton of pulp, a reduction of 92%. Comprehensive surveys of new recovery furnaces indicate that elimination of direct contact of flue gas with black liquor can reduce the emission rate from the recovery furnace to 0.01 lbs. of total reduced sulfur per A.D. ton of pulp. Miscellaneous sources such as the pulp washer hood vent, washer seal tank vent, oxidizer off-gas vent and knotter hood vent now constitute the major source of total reduced sulfur. Because of the large volume of these streams and low concentration of reduced sulfur compounds, treatment of these streams presents a difficult problem. Research and development efforts must now be concentrated on these sources.

10.2.6 RESEARCH ON CONTROL OF NSSC SOURCES

Little information is available about atmospheric emissions from NSSC process variations and about the operating and process variables that affect emissions. Data are lacking regarding the effect of NSSC liquor on emissions from NSSC-kraft cross-recovery. Some work has been done on processes for recovering NSSC liquor to prevent stream pollution, and this is reported here because of the possibility that the systems could be a source of atmospheric emissions.

Copeland, G. C. and Hanway, John E., Jr., THE TREATMENT OF NEUTRAL SULFITE SEMICHEMICAL SPENT LIQUORS IN A FLUIDIZED-BED REACTOR, TAPPI 47(6), 175-84A, (June 1964).

The experimental and commercial development of a fluidized-bed process, the Container Copeland process, for the disposal of spent NSSC liquor has given encouraging results in efficiently eliminating the usual disposal problems. A commercial unit capable of treating the effluent from a 130 ton/day NSSC pulp mill has been operated for over 1 year. The results of this operation indicated that complete oxidation of the organic content of the liquor can be accomplished under autogenous conditions at relatively low solids concentrations and that a pelleted granular residue of oxidized inorganic chemical containing essentially Na_2CO_3 and Na_2SO_4 can be produced. No evolution of sulfur-bearing gases, which could serve as a source of atmospheric pollution has been noted. It is believed that this system represents a significant improvement for the treatment and disposal of many types of pulp mill liquors. From a disposal standpoint, the process is simple, relatively foolproof, and economical.

Howard, W. C., A NEW AND ECONOMIC SOLUTION TO THE PROBLEMS OF STREAM AND AIR POLLUTION [IN THE PAPER INDUSTRY - THE FLUID-BED COPELAND PROCESS], Norsk Skogind 21 (4), 133-9, (April 1967).

The fluid-bed Copeland process for disposal (by combustion and oxidation) of spent liquors of various pulping processes (NSSC, Mg-base sulfite, kraft overload relief) and bark and sludge incineration is described in some detail with schematic drawings, along with applications of the fluid-bed reactor to lime burning (lime mud calcining), etc. 21 ref.

Klass, C. P., C[ONTAINER] C[ORPORATION OF] A[MERICA] SOLVES NSSC LIQUOR DISPOSAL PROBLEM [AT CARTHAGE, IND. MILL] WITH FLUID[IZED] BED REACTOR, Paper Trade J. 151 (13), 50-3, (March 27, 1967).

The Container Copeland Process plant at the mill for the combustion of NSSC spent liquor is described. The plant receives spent liquor from the first-stage vacuum washers at 9-10% solids. Triple-effect Horton long-tube vertical evaporators concentrate the liquor to a point where it will burn without additional fuel in the fluidized bed reactor. Air from the reactor goes to a 2-stage scrubber system. A dry pelletized product consisting of the residual inorganic salts (mainly Na_2SO_4 and Na_2CO_3) results from the operation. At present, this is being shipped to company kraft mills for use as make-up saltcake. Operation and economics of the process are discussed.

Williamson, D. F., Hough, G. W. and Mason, F. I., RECOVERY OF CHEMICAL IN COMBINED KRAFT AND NSSC PULP MILLS, TAPPI 52 (11), 2105, (November 1969).

The kraft/NSSC pulp production ratio for minimum capital expenditure of the NSSC mill depends on the chemical requirements of the kraft mill. With the processes available today, excess chemical from the kraft recovery can be converted to NSSC cooking liquor. Introduction of spent NSSC liquor to the kraft process is best carried out at the kraft digester, blow tank, or brown stock washers. Addition is also carried out at the evaporators, where pH of the combined liquors must be above 11 to avoid liquor precipitation and scaling. The use of 316 or 316L stainless steel tubes should be considered in the evaporators in order to keep down-time due to scaling to a minimum.

10.2.7 RESEARCH ON CONTROL OF SULFITE SOURCES

Only in recent years have process modifications been made to the sulfite process to reduce water pollution problems and recover heat and chemicals. The old calcium base has been replaced to some extent with soluble bases which are more amenable to recovery. Recent research has been directed toward recovery systems for the cooking liquor and improved absorption of SO_2. Complete information concerning gaseous emissions is still not readily available.

Ioffe, L. O., COMPUTATION OF THE FINAL DIGESTER BLOW-OFF IN THE SULFITE PROCESS, *Bumazh. Prom. No. 6*, 18-20, (June 1966).

During the final digester blow-off in the sulfite process 30-70% of the sulfur dioxide (I) and 10-20% of the heat are recovered. Moreover, the final blow-off determines to a large extent the content of the residual (I) in the spent liquor, hence the extent of pollution of the surrounding air during the discharge of the digester, and also the suitability of the SSL for biochemical processing. Despite the importance of this process, no computation means have been developed relating the temperature and pressure changes in the digester with the (I) content in the spent liquor. The author made an attempt to develop a computation method, based on the earlier devd. equation for the calculation of the amount of WV accompanying (I) during evaporation of the latter from aq. solutions and on the following assumptions: the liquid and the gaseous phases are in equil.; the solubility of (I) in the SSL is the same as in water; the SSL does not contain bound and easily split (I); and the volume of the SSL does not depend on the mat. of dissolved substances or on temperature. The equation relates the following parameters: the weight of spent liquor prior to blow-off *WIS*. (in kg.); the weight of WV accompanying (I), W_v; the ratio P/K characterizing the rel. volatility of WV and of (I) at a given temperature; and the content of (I) in the spent liquor prior to and after the blow-off X and X_1, respectively. Two difficulties were encountered in applying the equation, notably two unknowns (W_v and X_1), and the fact that the equation was devised for an isothermic process, while the blow-off is an adiabatic process, and hence, because of the dependence of P/K on temperature, by utilizing a second equation, that of the heat balance of the blow-off (assuming that the heat is consumed entirely for the evaporation of water and (I)). The second difficulty was eliminated by the method of successive approximations, to give data necessary for the determination of the temperature dependence of P/K and of the heats of evaporation of water and (I). Also, a method is presented for the calculation of pressure changes during the blow-off, by assuming the pressure to be equal to the sum of partial pressures of WV and (I). An example of computation for 1 ton wood is given, from which certain practical conclusions are drawn: The blow-off process should be controlled by the drop of temperature, not pressure. In order to lower the content of (I) in the SSL to 0.01-0.03%, a cooling of the digester by 20° C is sufficient [the residual (I) content will be also determined by its initial concentration in the liquor]. A lower starting temperature for the blow-off is more convenient, as it gives a lower residual (I) content. The calculations also show that the residual (I) content on the SSL can be made sufficiently low not to necessitate its additional removal prior to biochemical processing of the SSL.

Kann, F. and Fuchsel, R., COMPARISON OF THE DISTINCTIVE CHARACTERISTICS FOUND IN BURNING CONCENTRATED SPENT LIQUORS OBTAINED IN MAGNESIUM BISULFITE COOKS AND IN CALCIUM BISULFITE PULPING OPERATIONS, Papier 21 (4), 174-9, (April 1967).

After a brief review of current recovery systems, the basic differences required in burning the two types of SSL are described. Differences in digester operations, as well as in subsequent treatments are due to the fact that chemical recovery is not possible in the case of $CaHSO_3$ but is essential for $MgHSO_3$ spent liquors. Reasons for the more difficult techniques used in burning concentrated Mg spent liquors are described in detail together with the requirements for the construction of combustion chambers needed for Mg spent liquors. Difficulties have been overcome, thanks to studies made at the Lenzinger Zellulose and Papierfabrik in Austria; some of the experiments are described. The relationship between the brightness (whiteness) of the MgO ash and the temperature of the combustion chamber is emphasized. By maintaining a temperature of 1150°C an ash brightness of 54% was obtained. A unit recently installed at Lenzing permitted a combustion temperature of 1250°C, thus giving an ash brightness of 65%. After combustion the excess air was only 1.5% which was well within the limits required to prevent SO_2 from being oxidized to SO_3. Certain pitfalls are outlined and simple sketches are included.

Kruel, M., and Juntgen, H., DUST CLOUD REACTION OF DOLOMITE AND OTHER ALKALINE-EARTH COMPOUNDS WITH SO_2 IN WASTE GASES, Chem.-Ing.-Tech. 39 (9/10), 607-13, (May 24, 1967).

In a study of the desulfurization of waste gases through reaction with dolomite dust, a pilot plant was constructed in which the hot waste gases were passed through a heated reactor tube into which dolomite dust (or similar com. prod.) was blown. Measurement of the SO_2 content of the waste gases at various points along the reactor tube shows that the degree of desulfurization depends mainly on the temperature, the stoichiometric ratio of dolomite or other desulfurizer to SO_2, and the particle size and chemical composition of the desulfurizer. Reaction period was of secondary importance as long as a minimum of 1.5 seconds was exceeded. 6 ref.

Rusten, D., CONSTRUCTION AND OPERATION OF SCOTTISH PULP & PAPER MILLS, Norsk Skogind. 21 (11), 443-50, (November 1967).

An illustrated description is given of the layout, planning, and production operations of Scottish Pulp & Paper Mills at Fort William, including reafforestation of highlands for pulpwood, reasons for site selection, process water and effluent treatment, wood handling, pulping, bleaching, paper machine, and social importance of the new mill which is the first to use the Stora 2-stage high-yield sulfite process for an integrated operation. The flexible process gives bleaching-grade pulp for printing and writing papers without air pollution. Softwood is delivered by rail and road and purchased on a green weight basis, while hardwood chips are imported from North America. Wood storage is in chip piles. Five batch digesters of 225 cu.m. capacity each and a 5-stage bleach sequence (CEDED) are used. Bleached pulp is either baled at 50% dryness or pumped in slush form to the paper mill. Fine paper grades from 60 to 300 g./sq.m. basis weight are run on a 530 cm. wide fourdriner at speeds up to 450 m./minute. Total annual capacity is 80,000 tons of pulp and 40,000 tons of paper.

Smith, E. L., SULFITE PULPING AND POLLUTION CONTROL, Combustion 38 (12), 42-4 (1967).

Among the various means of disposing of sulfite pulping waste liquors, the least expensive method at present appears to be burning of the org. portion of the liquor. Many mills, in efforts to avoid the expenditures of a positive pollution control system, have resorted to makeshift arrangements such as lagooning to relieve their pollution problem. In the long run, this generally results in larger expenditures than if a positive pollution control system were installed initially. The development of the process for disposal of waste sulfite liquors by burning is traced and economic advantages to be gained by the installation of such a system are discussed. Finally, capital investment costs for such a system are considered.

Clement, J. L., MAGNESIUM OXIDE RECOVERY SYSTEM, TAPPI 49 (8), 127-A, (August 1966).

Equipment arrangements are presented to meet the requirements of a magnesia base pulp mill for complete recovery of heat and chemicals from spent sulfide liquor. Several designs of recovery boilers including alternate arrangements and designs of economizers and air heaters provide heat recovery in an integrated system. The cyclone direct-contact evaporator can recover heat to reduce the multiple-effect evaporator duty or increase the firing concentration of low heat value liquor. Heat recovery can be increased further by utilizing the low-level heat in the gas for production of hot process water. Boiler design can incorporate auxiliary fuel firing to assure steam production independent of liquor availability. Recovered magnesium oxide is used to remove 95% + sulfur dioxide from combustion gases in a Venturi absorption system to prepare acid at a concentration required by the pulp mill. Thermal performance and horsepower requirements for two pulping techniques of diverse yield establish that recovery capacity and size are a function of the heat input and not related to pulp production. The capacity of a recovery system is about twice as large for a low-yield dissolving-grade pulp as for a pulp to be used in newspring furnish.

Votoupal, J., SOME REMARKS ON THE ECONOMICS OR EVAPORATION AND BURNING OF SPENT CALCIUM BISULFITE LIQUORS, Papir Celuloza 22 (7), 193-8, (July 1967).

A system for evaporation and burning of Ca-base SSL was installed in 1966 at the Southern Czechoslavakian Mills. The evaporator has a capacity of 47-50 tons evaporated water/hr., and the two boilers for joint burning of the evaporated liquor and brown coal produce 75 tons stream/hour, the steam having a pressure of 64 atm. and a temperature of 450°C. The equipment includes a distillation column for the recovery of sulfur dioxide. The wash waters go directly to the evaporator. Considering that in the evaporation and burning of Ca-base liquor, the base is not recovered, the economic efficiency of the process is lower than in the case of other spent liquors, and calculations of the economic justifications must be based on the amount of sulfur dioxide and heat recovered and the amount of solid fuel saved. The author discusses the factors affecting the efficiency of the process, such as the concentration of the spent liquor prior to evaporation, the solids content of the liquor/ton pulp, the heat content of the liquor, the type of evaporation equipment used (vacuum or back pressure), and the type of fuel burned jointly with the liquor (coal of various types or oil). Graphs are presented illustrating the relation between the amount of water evaporated/kg. solids and the degree of liquor concentration;between the spent liquor solids and the pulp yield; between the concentration of the liquor and its heat content; between the amount of fuel saved and the spent liquor solids content when different types of evaporators are used; and between the evaporation efficiency and the concentration of liquor to be evaporated. Also given are diagrams of the equipment installed at the Southern Mills and of the Ramen system. It is pointed out that these considerations should be regarded as a general guide for economic calculations. A more precise evaluation must be based, in each individual case, on local conditions. 7 ref.

Copeland, G. G. and Overall, J. E., ELIMINATION OF SULFITE MILL WASTES BY FLUID[IZED] BED TREATMENT, Am. Paper Ind. 49 (3), 41-2, 45-9, 51, (March 1967).

The fundamentals of the Container-Copeland process are reviewed. Although the process was originally developed for the disposal of NSSC spent liquor, various modifications have been developed which permit its application in disposal of spent liquors from Mg and NH_3 base sulfite pulping, in processing kraft liquor recovery system overloads, and in the incineration of waste bark and paper machine white water sludge. Some cost data are cited on savings resulting from the use of the process.

Erdman, A., Jr., APPLICATION OF FLUIDIZED BED PROCESSING TO SPENT SULFITE LIQUOR COMBUSTION, TAPPI 50 (6), 110-12A, (June 1967).

SSL has long been a severe source of pollution. The SSL combustion system represents an economical method of abating both water and air pollution by converting the SSL to a granular inorganic solid and a clean, dust-free, odorless exhaust gas. In most cases, complete or partial chemical recovery is possible, or a salable product can be made which will pay for part of the operating costs of the system. Still more attractive is the fact that return on investment becomes an attainable asset when chemical recovery is coupled with other recovery devices, such as high- and low-level heat recovery.

Copeland, G. G., Hanway, J. E., Jr., Container Corporation of America, FLUID BED RECOVERY FOR FRANCONIA, Pulp Paper 42 (37), 29-31, (September 9, 1968).

The Copeland fluidized bed recovery system installed for chemical recovery at the company's sulfite pulp mill at Lincoln, New Hampshire, is described. When the conversion from ammonium-base to Mg-base pulping is effected, the system will recover both Mg and S.

Moody, Dennis M., BLOWPIT GAS RECOVERY WITH A SINGLE BLOW STACK SYSTEM, TAPPI 52 (3), 448, (March 1969).

A single blow stack system for the recovery of blowpit vent gases was designed and installed in the summer of 1966, replacing multiple wooden blow stacks. It consists of a stainless steel stack connected to the six blowpits by a header system. The stack acts as a scrubbing column, condensing steam and recovering sulfur dioxide from blowpit gases for reuse. The system is designed to operate at high flow rates and low pressure drops. Water is sprayed counter-currently to rising gases over specially designed stainless steel and wood packing. Water flow control is based on gas temperature and pressure. The system is 98% efficient in sulfur dioxide recovery and has resulted in both improved sulfur dioxide and heat recovery. Exit gases average about 1400 ppm SO_2.

Leitner, G. F., SPENT SULFITE LIQUOR EVAPORATORS - DESIGN AND PERFORMANCE, TAPPI 52 (7), 1296 (July 1969).

One of the main considerations in selecting a pulping process is the means of spent liquor recovery or disposal. The sulfite pulping process has some important advantages over kraft pulping, but until recent years its progress has been retarded by the inherent problems connected with the spent liquor. Six processes for treatment of spent sulfite liquor have been developed to the point of commercial use. All six have one thing in common: they require concentration by evaporation as a preliminary step. Some significant improvements have been made in recent years in evaporators for concentrating spent sulfite liquor. These have been in the area of scale control. These plants now operate continuously, whereas early designs experienced major operating difficulty in control of scale formations which caused frequent shutdowns. A new system being tested for use as a preconcentrator for very dilute wash water, reverse osmosis, is also described.

Clement, J. L. and Sage, W. L., AMMONIA-BASE LIQUOR BURNING AND SULFUR DIOXIDE RECOVERY, TAPPI 52 (8), 1449 (August 1969).

The use of ammonia-base for sulfite pulping requires consideration of waste liquor burning and sulfur dioxide combustion product recovery. Burning tests in a pilot unit demonstrate liquor can be burned at stable combustion conditions without supplementary fuel where the solids content of the liquor exceeds 50% and air temperature 550°F, and establish parameters for the projected design of a commercial liquor atomizer and water-cooled furnace to burn ammonium liquor. Reported sulfur dioxide absorption experience provides information to design a system for sulfur dioxide at a temperature of about 100°F; more economical design at the flue gas dew-point temperature requires additional knowledge of the effect of temperature on absorption system parameters.

10.2.8 RESEARCH NOT REPORTED IN THE LITERATURE

In addition to the foregoing, NCASI has identified the following categories of research or specific projects which presently are under way in the industry. Results may or may not be reported eventually in the open literature. It is not possible at this time to define the scope of work more completely nor to indicate the level of effort.

a. Completion of miscellaneous kraft emission source inventories at several mills, concentrating on brown stock washer, seal tank and knotter vents, and black liquor oxidation tower off-gases, to determine their relative importance as reduced sulfur compound emission sources. This program is being expanded to cover a large group of kraft mills with the knowledge that changes in recovery furnace systems definitely will result in greater attention being focussed on these miscellaneous sources.

b. Determination of the relation between pulping temperature sulfidity and sulfur emission at the digestor and evaporator.

c. Gas chromatographic identification of evaporator non-condensible and recovery furnace organic compound emissions.

d. Completion of the investigation of relative importance of the kraft recovery furnace and direct contact evaporator as reduced sulfur emission sources under varying conditions of furnace loading and operation, and degree of black liquor oxidation.

e. Determination of nitrogen and sulfur oxides emission levels for recovery furnaces.

f. Determination of particulate emission levels and characteristics for waste wood fired pulp mill power boilers.

g. Examination of recovery furnace operating variables including air supply and distribution, and liquor droplet size to develop furnace operating procedures which minimize internal process emissions.

h. Comprehensive review of black liquor oxidation technology leading to pilot testing of proprietary devices such as the spiral oxidizer, and multistage oxidation using tonnage oxygen for polishing purposes.

i. Review of emission control technology for lime kilns and bark-fired boilers.

j. Review of industry practice in Thermal oxidation of non-condensible gases from digestors and evaporators.

k. Evaluation of Scandinavian recovery furnace system evaporation features and their limited application in the United States specifically for sulfur odor emission control.

l. Examination of alternate particulate emission control systems for the recovery furnace, including bag filtration and electrostatic pre-agglomeration followed by wet scrubbing.

m. Evaluation of several techniques for scrubber recovery of SO_2 from sulfite pulpmill furnaces as well as NSSC mill power boilers to reconstitute sulfite pulping code liquors.

n. Development of high efficiency particulate collection systems for waste wood fired pulp mill power boilers, including scrubbing and electrostatic precipitation.

o. Cryogenic separation of odorous materials from kraft recovery furnace stacks and other process emission sources.

p. Stripping of evaporator condensates followed by activated carbon adsorption of odorous materials on activated carbon.

q. Catalytic and alkaline scrubbing and electrostatic precipitation as means for reducing H_2S content of kraft recovery furnace gases.

r. Use of fluidized bed techniques to modify the kraft chemical recovery process through substitution of an oxidative phase for the conventional smelting phase.

10.3 COST AND EFFECTIVENESS OF EMISSION CONTROL

During the course of this study, a dearth of information was noted on cost and relative effectiveness of a variety of control equipment for removal of gases, particulates, and combinations of the two. Reliable information was obtained on costs from some mills. Most mills, however, do not maintain their cost data in a manner which makes the information readily available for individual items of equipment. Little information in this category was noted in the published literature.

Kleinegger, J. C., RELATIVE ABSORPTIVE EFFICIENCY OF PACKED TOWERS IN MAGNESIUM ACID BISULFITE PRODUCTION, TAPPI 52 (7), 1291, (July 1969).

Two similar magnesium acid bisulfite absorption trains are compared and evaluated. The first system is a conventional series of four countercurrent packed towers using 6 X 6 in. cross partition packing throughout. The second system is a series of four towers, with the last three towers of the acid plant using 3 1/2 in. Pall rings, rather than cross partition rings. Development of the concept of mass transfer effectiveness is presented and applied to the two absorption systems. In each tower utilizing 3 1/2 in. Pall rings the height of an overall gas transfer unit is demonstrably less than for the comparable tower using 6 X 6 in. cross partition packing.

Arhippainen, B., and Westerberg, E. N., KRAFT ODOR CONTROL: ITS EFFECT ON MILL OPERATING PARAMETERS AND COSTS, Pulp Paper Mag. Can.69 (8), 65-70, (April 19, 1968).

This rev. discusses current knowledge on kraft odor control with emphasis on Scand. conditions and experiences; effects of an odor control installation on mill conditions (process S. equip., S losses, operating costs, etc.) and mill environment (attitude of people); and recovery boiler systems without and with direct contact evapn. and with or without addnl. odor control equipment (comparing Scand. to N. Am. practices). The two systems are believed to be competitive, but cost comparisons between the two countries must be modified to fit local conditions. 9 ref.

Willett, H. P., CUTTING AIR POLLUTION CONTROL COSTS, Chem. Eng. Progr. 63 (3), 80-3, (March 1967).

The costs of air pollution control can be drastically reduced by design innovations in the basic process which causes the pollution. Several examples are presented which show that substantial savings are possible by rel. inexpensive changes. For example, in the paper ind., the amt. of H_2S released to the atm. by combustion of the black liquor in the recovery furnace can be reduced greatly, if prior to combustion, the black liquor is oxidized with air.

10.4 SAMPLING AND ANALYTICAL TECHNIQUES

Much progress has been made since the early 1950's in sampling and analytical techniques for both gases and particulates. Time consuming wet chemical methods have been replaced by more sensitive and efficient techniques involving gas chromatography, coulimetry, UV spectroscopy, and IR spectroscopy. Progress has been made in both ambient air and source monitoring. Despite the progress, however, it is obvious that the available methods and instrumentation have not achieved the state of reliability and simplicity needed for continuous application in the field. Much of the work reported in the literature is applicable to kraft sources and the environment surrounding kraft mills. Although some of these procedures are applicable as well to sulfite and NSSC sources, but many are not. Reliable, standardized techniques for both gases and particulates for both ambient air and source monitoring are still the top research need.

Hendrickson, E. R., Walker, C. G., and Chapnerkar, V. D., IDENTIFICATION OF NON-SULFUR ORGANIC COMPOUNDS IN STACK GASES FROM PULP MILLS, Am. Ind. Hyg. Assoc. J. 24, 121-6, (March-April 1963).

Objectionable odors of stack emissions from pulp mills have been traditionally assocd. with S cpds. Concns. of identified cpds. are not considered dangerous to health of the community. In this study of stack gases, qual. identification was made of the presence of: benz[a]-anthracene, benzo[a]pyrene, benzo[e]pyrene, benzo[g, h, i]perylene, chrysene, coronene, fluoranthene, and pyrene. Tentatively identified were: anthanthrene, anthracene, phenanthrene, and vanillan [sic]. 9 ref.

Lur'e, Yu. Yu., Alferova, L. A., and Titova, G. A., ANALYSIS OF KRAFT PULPING EFFLUENTS, Zavodsk. Lab 29 (4), 412-15, (1963).

A method is described for the anal. of kraft mill effluents, which makes possible direct detn. of H_2S, MeSH, Me_2S, and Me_2S_2. A stream of CO_2 is passed through an acidified sample of the effluent and the components, entrained by the gas, are successivley absorbed in appropriate solns. Thus, H_2S is absorbed into an acidic soln. of $CdCl_2$, MeSH, and Me_2S_2 (the latter after conversion into MeSH by hydrogenation) into an alk. soln. of $CdCl_2$, and Me_2S into a 6% soln. of $HgCl_2$. The H_2S and MeSH are detd. iodometrically, Me_2S gravimetrically. The detn. of Me_2S_2 presents certain difficulties, due to its low volatility (it requires longer time of blowing CO_2) and retention in the absorption vessels prior to hydrogenation. For this reason, it is recommended that Me_2S_2 be blown, after the anal. is completed from the absorption vessels. The method was appl. to the anal. of effluents from a black liquor regeneration process. The results of the anal. are given. 4 Ref.

Suzuki, Y., Nishiyama, K., Oe, M. and Kametani, F., STUDIES ON THE PREVENTION OF PUBLIC NUISANCE BY THE EXHAUST GASES FROM THE KRAFT PULP MILL, Tokushima J. Exptl. Med. 11, 120-6, (1964).

Anal. of the exhaust gases from the kraft pulp mill showed the flg. to be present: 0.259 g./.^{3} of Na sulfate, 750 ppm of hydrogen sulfide, 196 ppm of sulfur dioxide, and org. cpds. of S. The org. S cpds. included the flg. in order of amt. present: methyl mercaptan, dimethyl sulfide, isoprophy mercaptan, dimethyl disulfide, propyl mercaptan or ethyl methyl sulfide, diethyl sulfide, and ethyl mercaptan. The concn. of dimethyl sulfide was 8.7 ppm. Org. S cpds. in the gas in the upper part of the Jansson screen were of the same cpn. as those in the stack gases, but the arrangement of the constituents in order of amts. present were different. All of these gaseous S cpds. have offensive odors and characterize the exhaust gases from a kraft pulp mill.

Risk, J. B., and Murray, F. E., CONTINUOUS RECORDING OF SULFUROUS GASES CONCENTRATIONS IN FLUE GASES, Can. Pulp Paper Ind. 17 (10), 31-4, (October 1964).

Methods of measuring the concn. of hydrogen sulfide and sulfur dioxide in flue gases are revd. and the devt. of a new method based on the use of a com. UV analyzer is described. The new method permits the continuous and reliable measurement of hydrogen sulfide content in flue gases of varying cpn. and contg. sulfur dioxide on a com. basis.

Thomas, Edgar W., DIRECT DETERMINATION OF HYDROCARBON SULFIDES IN KRAFT GASES BY GAS-LIQUID CHROMATOGRAPHY, TAPPI 47 (9), 587-8, (September 1964).

A rapid method of sampling and analg. kraft gases for hydrocarbon sulfides has been devd. by the use of a gas chromatograph. The use of a flame ionization detector with its high sensitivity to hydrocarbons and its insensitivity to water enables samples of gases to be taken directly from the stream and anald. It is not necessary to conc. or dry the samples as would be the case if a thermal conductivity detector were used. All concnts. of mill gases have been anald. and tables are given for the various sampling points. 7 Ref.

Adams, D. F., Koppe, R. K., and Tuttle, W. N., ANALYSIS OF KRAFT MILL, SULFUR-CONTAINING GASES WITH GLC IONIZATION DETECTORS, J. APCA 15 (1), 31-3, (1965).

Simulated process gas mixtures comprising H_2S and CH_3SH were comparatively separated with five types of detectors in chromatographic columns. Minimum detectable concentrations of CH_3SH was 0.5-1.0 ppm with flame ionization and that of H_2S was 3.0 ppm with coulometric titration. Electron capture, thermionic emission, and thermal condensation were also evaluated.

Adams, D. F., Jensen, G. A, Steadman, J. P., Koppe, R. K., and Robertson, T. J., IMPROVED SULFUR-REACTING MICROCOULOMETRIC CELL FOR GLC, Anal. Chem. 38 (8), 1094-6, (1966).

The sensitivity of the cell configuration of a common transistorized coulometer was modified by converting to a Br cell with the reference electrode in direct contact with the titration cavity was 30 times greater than the original cell. The column effluents can be oxidized to SO_2 or reduced to H_2S prior to introduction into the microcoulometric cell. Reduction to H_2S provided a four-fold increase in sensitivity over oxidation to SO_2.

Adams, D. F., and Koppe, R. K., A MANUAL FOR DIRECT GAS CHROMATOGRAPHIC ANALYSIS OF SULFUR GASES IN PROCESS STREAMS, NCSI Technical Bulletin 30, (1966).

Rayner, H. B., Murray, F. E., and Williams, I. H., STUDIES ON THE GAS-CHROMATOGRAPHIC ANALYSIS OF KRAFT MILL SULFIDES. (2) DETERMINATION OF MICROGRAM QUANTITIES OF METHYL MERCAPTAN, METHYL SULFIDE, AND METHYL DISULFIDE IN AQUEOUS SOLUTION, Pulp Paper Mag. Can 68 (6), (June 1967).

An anal. method has been devd. for the detn. of MeSH, Me$_2$S, and Me$_2$S$_2$ in aq. soln. Precision of the procedure is within 5%, and a minimum of about 10 parts per billion of each of the sulfides in water can be estd. The method is useful in assaying water streams from a kraft pulp mill for these odorous cpds. (12 ref.

MacDonald, G. L., W.C.F.P. Ltd., and Crofton, B. C., MONITOR CUTS RECOVERY BOILER STACK LOSSES, 50%, Pulp Paper 40 (17), 39-41, (April 25, 1966).

An instr. for the continuous monitoring of Na losses in a kraft black liquor recovery boiler stack is described. The instr. operates by measuring the conductivity of a continuous sample soln. obtained by autom. mixing a const. flow of flue gases with a const. flow of water. The monitor facilitates immediate correction of elec. and mech. failures of the electrostatic precipitators or the like used in chemical recovery from the flue gases.

Banciu, I., DETERMINATION OF SODIUM SALT LOSSES IN THE FLUE GASES OF SULFATE RECOVERY FURNACES, Celuloza Hirtie 15 (7), 253-7, (July 1966).

A method of sampling, anslg., and calcg. Na salt losses from kraft recovery boiler flue gases is presented which permits the dust-retention capacity of electrostatic filters (precipitators) to be monitored and controlled.

Adams, D. F., and Koppe, R. K., DIRECT G[AS] L[IQUID] C[HROMATOGRAPHIC], COULOMETRIC ANALYSIS OF KRAFT MILL GASES, J.APCA 17 (3), 161-5, (March 1967).

A new Br microcoulometric titration cell (cf. A.B.I.P.C. 38: abstr. 862) was used with a commercially available microcoulometer for the detection and anal. of S-contg. gases in various kraft pulp mill emissions. Sepn. of the constituents of the gaseous mixts. emitted from mill sources (such as the recovery furnace, digesters, lime kiln) is accomplished on a 8ft. X 3/16-inch. stainless steel column packed with 10% Triton X-305 on 60-80 mesh Chromosorb G. The column is isothermally operated at 30°C. for 4-6 min. and then rapidly heated to 70°C. The exact program is varied with the type of sample anald. Each source gas is initially screened by direct injection of 0.01-0.1 ml. of gas to det. whether or not disproportionately large concns. of one or more components are present. Appropriate sample vols. are then selected to provide "on-scale" recorder peaks for the major constituents. Elution times for the major constituents are noted so that these cpds. can be vented at the proper time flg. injection of large sample vols. (up to 10 ml.) when detecting and analg. minor constituents. Venting of the high concn. cpds. is necessary when analg. large vol. samples to maintain near equil. titration conditions in the microtitration cell. 12 Ref.

Bethge, P. O., and Ehrenborg, L., IDENTIFICATION OF VOLATILE COMPOUNDS IN KRAFT MILL EMISSIONS, Svensk Paperstid 70 (10), 347-50, (May 31, 1967).

In order to identify cpds. contributing to kraft mill odors, qual. anal. were made of digester relief, blow gases, and raw sulfate turpentine, using gas chromat. and-where necessary-mass spectrometry. In the most volatile fractions, 25 cpds. were identified in addn. to terpenes. Tabular data given include rel. retention times. 3 Ref.

Cooper, S. R., and Haskell, C. F., CUTTING CHEMICAL ASH LOSSES IN A KRAFT RECOVERY SYSTEM, Paper Trade J. 151 (13), 58-9, (March 27, 1967).

Continuous monitoring of recovery boiler stack gases for dust particles at the Oxford Paper Co, Rumford [Me.] kraft mill is used in controlling burning and electrostatic precipitator operation for minimum dust losses. The stack effluent measuring system includes a Bailey Meter bolometer transmitter and light source operating in conjunction with a receiver-recorder. The data obtained are used in adjusting recovery boiler combustion conditions and performing precipitator maintenance for minimum stack losses. Tests have shown the efficiency of the precipitator to drop from 95% at its rated load of 300 t./day to 51% at a load of 370 t./day.

Walther, J. E., and Amberg, H. R., CONTINUOUS MONITORING OF KRAFT MILL STACK GASES WITH A PROCESS GAS CHROMATOGRAPH, TAPPI 50 (10), 108-10A, (October 1967).

A "320 Beckman" process gas chromatograph was evald. intermittently on a recovery furnace for about 3 months. The instr. was installed to obtain information about furnace operation, esp. the emission of S cpds., and to det. whether it can be used as a tool for closer control of malodorous flue gases. During the 3-month trial period, several thousand samples were taken and anald. for H_2S, SO_2, and MeSH. Fluctuations in H_2S concns. from 100 to 400 ppm by wt. were recorded during normal operation of the recovery furnace. "Blackouts" (loss of fire) were preceded by high H_2S concns. The H_2S concn. appeared to be a more sensitive parameter of furnace operation than oxygen and combustible concns. It appears that the process chromatograph may be used as an indicator of furnace operation efficiency. 3 Ref

Adams, D. F., Young, F. A., and Luhr, R. A., EVALUATION OF AN ODOR PERCEPTION THRESHOLD TEST FACILITY, TAPPI 51 (3), 62-7A, (March 1968).

The design of a facility for the study of odor perception and objectionability thresholds within a large human population is described. A dynamic system of odor generation was used to provide several test atmospheres in the ppb concn. range within 6 exposure chambers. Panelists were consecutively exposed to the 6 identical chambers, each contg. a different concn. of the same cpd. (hydrogen sulfide) or purified air. Test atms. were presented in ascending, descending, or random order and ranged from undetectable to objectionable for most panelists. The panelists reported for each chamber, whether or not an odor was detected and, if so, whether it was pleasant or unpleasant. In addition, each panelist provided comprehensive personal information including age, sex, smoking habits, respiratory abnormalities, occupation, and population range of residence. The variability of individual response was evald. for 11 trained panelists through repeated sequences over a period of several days. The normal variation in threshold for each individual and the entire test panel are discussed. These data form a statist. basis for exam. of the response of nearly 6000 untrained subjects who were exposed only once to 5 concns. of a single cpd. in the 6 chambers. 4 Ref.

Theon, G. N., DeHaas, G. G, and Austin, R. R. INSTRUMENTATION FOR QUANTITATIVE MEASUREMENT OF SULFUR COMPOUNDS IN KRAFT GASES, TAPPI 51 (6), 246-9, (June 1968).

Recording electrolytic titrator has been evald. in quant. detns. of S. dioxide, H sulfide, EtSH, MeSH, org. sulfide, and residual S concns. After slight modification, the instr. gave rapid and reliable anal. of ambient air and samples drawn from kraft recovery furnace ducts, oxidn. tower vents, and lime kiln stacks. By selecting the proper setting, H sulfide concns. from 10 ppb to 800 ppm can be detd. within 7-10 min. per sample. Anal. can be performed in the lab. or at the sample-collection point, since the app. is portable. 4 Ref.

Walther, J. E., and Amberg, H. R., MOBILE LABORATORY FOR SOURCE-SAMPLING KRAFT MILL EMISSIONS, TAPPI 51 (11), 126-29A, (November 1968).

A mobile lab. contg. thermal cond. and flame ionization detectors and gas chromatographs for the analyses of malodorous emissions from kraft mills was constructed. The analyses conducted at a kraft mill showed that the malodorous emissions from the recovery furnace and direct contact evaporator can be reduced to < 3 ppm. Black liquor oxidn. efficiency > 95% combined with proper operation of the furnace was necessary to achieve this low level.

DeChoudens, C., QUANTITATIVE DETERMINATION OF SULFUR DIOXIDE AND HYDROGEN SULFIDE BY SPECTROPHOTOMETRY IN THE GASEOUS EFFLUENTS OF RECOVERY BOILERS IN A SULFATE PULP MILL, ATIP 22 (2), 113-21, (1968).

An app. is described for sampling the stack gases from pulp mills. Particulate matter in the effluent is removed, the temp is lowered, condensibles and water are removed, and the gas is metered to the colorimetric anal. system. H_2S and SO_2 are each detd. with a precision of 10%. The effects of temp. and concn. of the anal. solns. on the calibration curves are reported.

Adams, Donald F., ANALYSIS OF MALODOROUS SULFUR - CONTAINING GASES, TAPPI 52 (1), 53, (January 1969).

The current state of the art for analysis of five major sulfur-containing gases in ambient air-sulfur dioxide, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide-is presented, inherent errors described, and improvements proposed. Variability in the cadmium hydroxide slurry-methylene blue procedure for hydrogen sulfide is eliminated by addition of 1% STRactan 10 to the absorbing media. Errors in the lead acetate tape technique for determination of hydrogen are restated. The potential interference from dimethyl disulfide in the colorimetric determination of methyl mercaptan is defined. An automatic technique for separation and analysis of the five sulfur-containing gases is described.

Bamesberger, W. L. and Adams, Donald F., FIELD COMPARISON OF THE COULOMETRIC, COLORIMETRIC, AND LEAD ACETATE TAPE ANALYSIS METHODS FOR SULFUR-CONTAINING GASES, TAPPI 52 (7), 1302, (July 1969).

A continuous, microcoulometric analyzer, utilizing preselective filtration, has been used for a field study of the varying atmospheric concentrations of sulfur dioxide, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide in the vicinity of a kraft pulp mill. The microcoulometric analyzer was operated on a 5-min. sequence for each of the five sulfur-containing compounds and a 5-min. instrument blank, thereby yielding a complete analysis cycle every 30 min. Another coulometric analyzer with lower sensitivity was used as a total sulfur gas analyzer. Comparative 2-hr. average data were obtained for hydrogen sulfide and sulfur dioxide by using midget impingers in a sequence sampler. Chemical analyses were conducted by the cadmium hydroxide - STRactan - methylene blue and modified West-Gaeke methods, respectively. A third comparison for hydrogen sulfide was obtained by using the lead acetate tape method. The data show agreement for hydrogen sulfide by the microcoulometric and cadmium hydroxide-STRactan-methylene blue methods but not with the lead acetate tape technique. Agreement was also obtained for sulfur dioxide by the microcoulometric and modified West-Gaeke methods, although all observed sulfur dioxide levels were near the sensitivity limits for these methods.

Theon, G. N., DeHass, G. G, and Austin, R. R., CONTINUOUS MEASUREMENT OF SULFUR COMPOUNDS AND THEIR RELATIONSHIP TO OPERATING KRAFT MILL BLACK LIQUOR FURNACES, TAPPI 52 (8), 1485, (August 1969).

A continuous instrument has been designed and built to measure sulfur dioxide and reduced sulfur compounds in the parts-per-million and parts-per-billion ranges. The instrument has been placed in operation on several black liquor recovery furnaces before the direct contact evaporator. Operation parameters under most possible conditions have been measured and correlations between sulfur dioxide and reduced sulfur compounds have been made. Steam production and degree of smelt reduction have also been determined in relation to the concentrations of the sulfur compounds.

Thoen, G. N., DeHaas, G. G., and Baumgartel, F. A., CONTINUOUS SULFUR DIOXIDE ANALYZER AND ITS APPLICATION TO SULFITE RECOVERY EMISSIONS, TAPPI 52 (12), 2304- (December, 1969).

A continuous recording SO_2 analyzer with a variable range of measurement has been developed. The equipment is simple and corrosion-proof. The principle of operation is ultraviolet emission at specific SO_2 absorption. Water vapor and other compounds do not interfere. A unique sampling system has been devised to assure continuous, accurate sampling across the full duct so that averages need not be taken. Measurement with subsequent control can minimize SO_2 losses from the absorption towers of the sulfite recovery system.

Tretter, V. J., USE OF CONTINUOUS MONITORS OF SODA LOSS AND MALODOROUS SULFUR LOSS IN PROCESS CONTROL, TAPPI 52 (12), 2324-, (December 1969).

Continuous monitors were used to measure soda loss and malodorous sulfur loss. Normally both instruments monitor the main stack, which contains combined flue gases from three recovery furnaces and three lime kilns. The sulfur monitor has been found to be effective for indirectly and continuously monitoring the efficiency of the black liquor oxidation system. The monitor has also been used to characterize the contributions of the recovery furnace, cascade evaporators, recovery scrubbers, and lime kilns to total malodorous sulfur loss. The soda loss monitor provides accurate soda loss data and will detect firing rate changes in the furnace and precipitator malfunctions. Continuous monitors proved to be superior to wet sampling methods and have adaptability to process control.

10.4.1 RESEARCH NOT REPORTED IN THE LITERATURE

In addition to the foregoing, NCASI has identified the following categories of research or specific projects which presently are under way in the industry. Results may or may not be reported eventually in the open literature. It is not possible at this time to define the scope of work more completely nor to indicate the level of effort.

a. Mill-scale evaluation of sodium-specific ion electrodes conductivity cells, flame photometers and photoelectric cells as means for continuously monitoring recovery furnace particulate emissions as a means of reducing such emissions through more effective operation of high efficiency particulate collection devices.

b. Improvement of techniques for sampling hot, wet, corrosive gas streams.

c. Examination of particulate collection efficiency of various emission source sampling procedures (particle filters and scrubbers in various combination and retention capabilities.

d. Selection of optimal analytical procedures for determination of residual sulfide levels following black liquor oxidation.

e. Investigation of new excess oxygen analyzers for use in recovery furnaces and lime kilns for combustion process control

f. Development of techniques for scanning recovery furnace smelt bed for combustion process control.

g. Differentiation of reduced sulfur compounds using various filter systems in conjunction with coulometric, flame photometric and infra red absorption instruments to achieve sensitivity in the ambient ppb range.

h. Selection and development of suitable sulfur oxides analyzers for use in sulfite pulping inventory studies.

i. Development and application of organoleptic techniques for evaluation of emission control systems.

j. Development of techniques for optimal design of mill ambient air quality monitoring programs.

10.5 CONTROL EQUIPMENT DEVELOPMENT

Control of most emission in the industry is brought about by add-on devices. The state of the art is described in Chapters 5 and 6. Research in the past has been concerned mostly with recovery of particulates. In recent years more effort is being devoted to reduction of odorous sulfur gases. Generic types of collectors are well known, but the effectiveness of scrubbing liquids in removing the various gases encountered is not well known.

Maksimov, V. F., and Torf, A. I., JET-TYPE APPARATUS FOR THE PURIFICATION OF FLUE GASES, Bumazh. Prom. 39 (5), 6-7, (May, 1964).

An exptl. jet-type gas scrubber for the removal of dust from flue gases of soda recovery furnaces was installed recently at the Segezha Combine. The principle of the scrubber operation consists in mixing the gases, in a vert. constricted tube, with a mist of water introduced, by means of mech. nozzles, under a pressure of 6-12 atm. Exptl. data are presented showing the dependence of the scrubbing efficiency of the app. on the flow rate of gases in the constricted part of the tube, the amt. of water fed into the tube, the conditions, the efficiency of dust removal was 96-97%, at initial dust concns. of up to 9.35 g./cu.m. 2 ref.

Maksimov, V. F., Torf, A. I., and Lesokhin, V. B., A JET FLUE GAS SCRUBBER FOR SODA RECOVERY BOILERS, Bumazh. Prom. 39 (11), 17-18, (Nov., 1964).

The gas scrubber described comprises four high-pressure (8-11 atm.) spray nozzles, distributed so that they form a circle, from which a stream of water is introduced into the path of the flue gas. The app. acts as an exhaust fan (by its sucking effect), as a scrubber to remove suspended solids and SO_2, and as a heat exchanger. At a water jet pressure of 10 atm. and a water flow rate of 13 cu.m./hr., the underpressure in the flue is up to 10 mm. H_2O. The water, by passing through the app., is heated to 60°C. (from about 2°), and the gases are cooled from 170-200° to 65-70°.

The efficiency of the scrubber is up to 96% with respect to solids particles, and 65-70% with respect to SO_2. The scrubber was installed at the Astrakhan board mill and was tested under ind. conditions.

Clark, J., HOW [PULP] MILLS USE [GAS] SCRUBBERS, Pulp Paper 39, (32), 31-3, (Aug. 9, 1965).

The author recommends the use of fiberglass-reinforced polyester for the construction of scrubbers. To handle corrosive matls., the entire system should be fabricated of corrosion resistant matls. The use of scrubbers in the recovery of sulfur dioxide, Cl, Cl dioxide, and in the control of discharge of mercaptans and hydrogen sulfide is discussed briefly.

Maksimov, V. F., Torf, A. I., and Lesokhin, V. B., TESTING OF A TWO-STAGE GAS SCRUBBER, Bumazh. Prom. 40 (10), 13-15, (Oct., 1965).

A series of ind. tests was performed to det. the efficiency of a two-stage gas scrubber mounted on a Tapella soda-regenerating boiler, and sprayed with black liquor. The scrubber (installed recently with the Tampella boiler at the Astrakhan pulp and board mill) is described and the results of the tests are tabulated. They include the cpn. of the gases before purification, the operating variables of the first and second purification stages, and the purification efficiency. The overall purification efficiency of the scrubber was up to 93.5% and its efficiency in absorbing sulfur dioxide and hydrogen sulfide was 93-95%.

Maksimov, V. F., Bushmelev, V. A., Torf, A. I., and Lesokhin, V. B., TESTING THE TURBULENT FLOW VENTURI APPARATUS, Bumazh Prom. 40 (5), 14-15, (May, 1965).

A turbulent-flow Venturi scrubber (TAV) was installed recently on the soda recovery boiler at the Kherson kraft mill, and was subjected to a series of tests to det. its efficiency. The TAV consists of a Venturi tube, spray tubes, and condensation trap. Black liquor is used as the spray liquor. According to exptl. data obtained SO_2 is absorbed to the extent of 96-98%, and the scrubber is equally effective in removing suspended dust particles. There was no evolution of H_2S or disturbances of the combustion process (e.g., a too low supply of O_2). Since in preliminary expts., carried out with model equipment at another mill, there was evolution of H_2S, this problem was further investigated. It was found that the black liquor of the Kherson mill contains considerably less residual Na_2S as compared with the black liquor used in model expts., due to lower sulfidity of the white liquor. In addn., the vacuum filters, used at the mill for washing pulp, promote a partial oxidn. of the black liquor, further reducing its Na_2S content. The purification of gases in the TAV scrubber was accompanied by addnl. evapn. of black liquor, caused by contact with hot gases at the throat of the Venturi tube. The TAV scrubber is thus also an effective heat exchanger. Other factors affecting the scrubbing efficiency of the app. are the flow velocity of the gases in the Venturi tube throat, the concn. of the black liquor, its amt. used for spraying, and its temp.

Shah, I. S., and Mason, L., NEW TWO-STAGE EVAPORATOR-SCRUBBER SYSTEM FOR EFFICIENT RECOVERY OF HEAT, FUME, AND DUST FROM RECOVERY BOILERS, TAPPI 50 (10), 27-32A, (Oct., 1967).

The 3 systems in prevalent use in N. Am. for heat and chem. recovery from kraft recovery furnaces (viz., the cascade-precipitator, cyclone-precipitator, and P-A Venturi evaporator-scrubber) are unable to meet the increased requirements for overall dust-collection and odor-removal efficiencies specified by recent federal, state, and local legislation and regulations. For this reason, a new 2-stage system comprising an S-F evaporator, an S-F scrubber as separator, and a cooler has been devd., which is said to offer higher thermal efficiency, comparable or greater dust-collection efficiency, minimum maintenance, and high flexibility of operation in that the evaporator performance is indep. of the scrubber's performance. The S-F Venturi scrubber can also be used as a single-stage system by mills considering a cyclone or cascade evaporator as a direct-contact evaporator as well as by mills about to replace their precipitator by a wet scrubber. In addn., 3 secondary scrubbing systems have been devd. (vis., cyclonic, S-F Venturi flg. a cascade-precipitator, and S-F Venturi flg. a P-A Venturi for improving dust-collecting and/or thermal recovery efficiencies in mills having a cascade or P-A Venturi System. The design and operation of these new systems are described and sketched. 4 ref.

Shah, I. S., NEW FLUE-GAS SCRUBBING SYSTEM REDUCES AIR POLLUTION, Chem Eng. 74 (7), 84-6, (March 27, 1967).

In the kraft pulping process, the burning of black liquor is a necessary step because it recovers heat and chemicals. However, this also releases dust and S-contg. gases into the atm. In a new Venturi scrubbing system (Chemical Construction Corp.) described, 99% of the dust is removed from the flue gases, and an improved oxidn. step greatly reduces the amt. of H_2S released to the atm. A process flowsheet is included.

Malarkey, E. J., and Rudosky, C., HIGH EFFICIENCY KRAFT MILL PRECIPITATORS, Paper Trade J. 152 (40), 57-8, (Sept., 1968).

A dry collection system for recovery boilers in kraft mills is compared with a dry-wet system. Although high efficiency electrostatic precipitators can minimize fall-out or snowing, the dry-wet system can virtually guarantee that it will not occur. Comparative installation and operating costs are presented.

Aho, W. O., THE JENSSEN EXHAUST SCRUBBER - AN EFFECTIVE AIR PROTECTION SYSTEM , TAPPI 52 (4), 620, (April 1969).

A system incorporating a bubble cap tray absorption column was designed and installed to recover sulfur dioxide from two Jenssen tower exhausts. With this system the exhaust gases are scrubbed with a sodium hydroxide-sodium bisulfite solution, and the resulting liquor is used in a neutral sulfite-chemimechanical pulping process. Potential problems stemming from sulfur trioxide and carbon dioxide in the gases were evaluated. Other types of scrubbers were examined. The design procedure for the scrubber is reviewed and a description of the recovery process is included. Both a source of air pollution and economic loss were eliminated.

10.6 PROCESS CHANGES AFFECTING EMISSIONS

Major, W. D., VARIATIONS IN PULPING PRACTICES WHICH MAY EFFECT EMISSIONS, in Atmospheric Emissions from Sulfate Pulping (E. R. Hendrickson, Ed.), April 1966.

Emissions from a kraft mill can be divided into two categories, gaseous and particulate. Malodorous emissions are subject to far less control and precision of analysis than particulate emissions. The magnitude of loss is more sensitive to operating variables, the chemistry is more complicated and the sources are more numerous. This discussion is concerned with the effect of operating variables on gaseous sulfur losses. Evidence is given which indicates that the wood species has a definite effect on the odor produced during kraft pulping. Cooking variables include: sulfidity of the white liquor, cooking time and cooking temperature. More recent cooking variables are: continuous vs. batch digestion and the use of black liquor dilution in the digester as a means of controlling the liquor-to-wood ratio. Multiple-effect evaporators are the second largest source of gaseous sulfur losses in the process. The high vacuums set up by condensers result in the release of low vapor pressure sulfur compounds. Operating variables in direct contact evaporation are: black liquor pH, sodium sulfide concentration, and percent CO_2 in the flue gas. Dust losses from the recovery furnace are controlled with either a Venturi scrubber or an electrostatic precipitator. Operating variables which influence the efficiencies of these two units are overloading, and the temperature of the flue gas. The key to the effect of operating variables on emissions from a kraft pulp mill is to recognize the degree to which the various steps in the kraft process are interrelated, especially in the case of gaseous sulfur losses.

Harkness, A. C., and Murray, F. E., GAS PHASE OXIDATION OF METHYL MERCAPTAN, Air & Water Pollution 10 (4), 245-51, (April, 1966).

The reaction between Me mercaptan and O in the gas phase has been examd. in temp. range 201-275°C. S. dioxide is the chief prod. of the reaction, being formed together with methane at the start of the reaction. Other prods. are carbon monoxide, carbon dioxide, H, HCHO, and MeOH. In the presence of excess O, complete conversion to S dioxide is obtained quickly at 275°C. At lower temps. and lower O content much of the S remains unaccounted for. In confirmation of previous work, the rate of reaction was found to be strongly accelerated by O and to be inhibited by mercaptan.

Fischer, H., THE CLAUS PROCESS AND ITS MODIFICATIONS, Chem.-Ing.-Tech. 39 (9/10), 515-2, (May 24, 1967).

The ever-increasing interest in pollution control has led to a re-exam. of the Claus process for the recovery of S from H_2S-contg. waste gases through the bauxite-catalyzed reaction of the waste gases with atm. O in a special combustion chamber. Various modifications of the process have been devd., some of which are specially designed for trg. the H_2S-contg. waste gases of a particular ind. (e.g., the petroleum ind., the pulp ind., etc.). Several Claus recovery systems are diagrammed, incl. 2 examples for pulp mill installation. 4 ref.

Murray, F. E., and Rayner, H. B., OXIDATION OF DIMETHYL DISULFIDE WITH MOLECULAR OXYGEN, Pulp&Paper Mag. of Can. 69 (9), 64-7, (May 3, 1968).

The rate and mechanism of oxidn. of dimethyl disulfide with oxygen in aq. NaOH was studied at temps. from 25 to 125°C. In this interval, the oxidn. rate is controlled by the O mass transfer rate, except at low disulfide concns. The reaction mechanism seems to involve alk. hydrolysis of the disulfide to form NaSMe (mercaptide) and NaOSMe (methanesulfensate) fld. by oxidn. of the MeSNa to disulfide while the MeSONa is oxidized to $MeSO_3Na$ (sulfonate) which is the primary end-prod. of the oxidn. These results indicate that the malodorous S cpds. in kraft mill condensates can be rendered rel. innocuous by oxidn. to methanesulfonic acid. For air pollution control, pure O in a pressurized reactor would be needed. (An air stream would strip much mercaptan and disulfide from the water before they could be oxidized). Although the methyl mercaptide ion in black liquor is readily oxidized to dimethyl disulfide, much mercaptan in com. plants is given off with noncondensibles from the multi-effect evaporators. This MeSH is probably formed from the disulfide during black liquor storage and evapn. as a result of alk. hydrolysis at the elevated temps. used. 10 ref.

Gullichsen, J., Saiha, E., and Westerberg, E. N., RECOVERY OF SODIUM-BASE PULPING CHEMICALS BY BICARBONATION AND CRYSTALLIZATION, TAPPI 51 (9), 395-400, (Sept. 1968)

A modified chem. recovery process is presented, based on reductive burning of spent liquor and carbonation of green liquor with CO_2-contg. flue gases. The precarbonated green liquor is reacted with Na bicarbonate at boiling temp., preferably in a slight vacuum, to liberate H_2S and form Na carbonate which can be crystd. simult. or sep. The bicarbonate needed is produced by carbonation of crystd. Na carbonate with flue gases. Both lab. and pilot-plant trials showed that a highly concd. pure H_2S gas and clean carbonate (monohydrate) crystals can be produced, and that carbonation of soda with flue gases yields pure cryst. bicarbonate. The process is suitable for chem. recovery and cooking liquor regeneration in both acid and alk. processes, and is ep. adaptable to cross-recovery operations. 8 ref.

Izumrudova, T. V., Parashina, F. I., and Shorygina, N. N., MODIFICATION OF SPENT SULFITE LIQUORS BY CHLORINATION, Bumzah. Prom. 43(11), 34, (Nov., 1968).

LSA isolated from a com. SSL from mixed Ca/Na base cook, and from a lab. cook of extd. sprucewood sawdust with a disulfite liquor contg. 8.5% sulfur dioxide, were dried over P pentoxide and anald. to det. their empirical formulas. The two prepns. which differed in their contents of S and C and contained no ash elts., were then chlorinated in an aq. medium and in carbon tetrachloride. Chlorination in the aq.medium was more extensive yielding derivs. with 13 Cl atoms/10 phenylpropane units. In the non-aq. medium, 6-8 Cl atoms were introduced/10 units. The S. content remained unchanged in all expts., but chlorination was accompanied by oxidn. (as evidenced by an increase of the O content) and by demethoxylation. Changes in the chm. cpn. of the LSA upon chlorination were confirmed by their IR spectra. Of pract. interest is the chlorination of the residual liquor from alc. fermentation of SSL. The chlorinated residual liquor is a surface-active agent stable in media contg. mineral cpds,; these props. make it esp. well suited for use as a drilling fluid additive and as a cement suspension stabilizing agent. 2 ref.

10.7 CHEMISTRY OF POLLUTANT FORMATION OR INTERACTIONS

For a complete understanding of the effect of pulp mill emissions on the environment and to provide a firm base for developing control technology, an appreciation of how the pollutants are formed is essential. Partly because of the unavailability of reliable analytical techniques, development of the required information was slow. It has only been in recent years that more complete knowledge of the chemistry and kinetics of odor formation from kraft pulping is developing. Reactions in the atmosphere after discharge are still largely unknown. The relationship between particulates and gases in odor transmission is also unanswered.

McKean, William T., Jr., Hrutfiord, Bjorn. F., and Sarkanen, K. V., KINETIC ANALYSIS OF ODOR FORMATION IN THE KRAFT PULPING PROCESS, TAPPI 48 (12),699-704, (Dec., 1965).

The kinetics of the consecutive formation of MeSH and Me$_2$S at const. liquor cpn. were detd. at several temps. using a novel gas anal. technique based on vapor-phase sampling. Comparative kraft cooks of softwoods vs. hardwoods shows that more org. S. cpds. are produced from hardwoods. During the alk. delignification of softwoods, the reactivity of lignin MeO groups is enhanced, which results in accelerated odor formation during the last phase of pulping. The activation energies of the reactions suggest that the formation of org. S cpds. may be substantially reduced by raising the reaction temp. and shortening the duration of the kraft cook. These findings suggest that kraft mills without odor problems should operate by maximizing cooking temp., minimizing cooking time and sulfidity, and improving oxidn. of black liquor early in the evapn. phase. Continuous digesters hold more promise than batch digesters. 27 refs.

Uchida, T., and Shirota, F., STUDIES ON VOLATILE MATTER IN KRAFT COOKING, (1) VOLATILE MATTER IN THE KRAFT COOKING OF HARDWOODS, J. Jap. TAPPI 19 (10), 479-87, (Oct., 1965).

The volatiles obtained from ind. kraft cooks of hardwoods (compared to softwoods) were factionally distd. and examd.

for b.p., and sp.gr., refractive index, optical rotation, and IR spectra. The crude condensed volatiles differed considerably in phys. props. from those obtained in softwood kraft cooks. The essential oil components in the crude condensate of hardwoods had rel. high b.p. Colored and malodorous cpds. of low b.p. (aldehydes, ketones, alcs., furans) were found in hardwood volatiles, but not in softwood condensates. The α-pinene content was ca. 40%, i.e., somewhat less than in the crude condensates from softwoods. Components identified in the rectified fractions included mixts. of alcs., ketones, aldehydes, furan, α-pinene, dl-limonene, cadinene, and azulene.

Sokolva, O. I., and Maksimov, V. F., EQUILIBIRUM CONCENTRATIONS OF S-CONTAINING GASES IN RELATION TO DEODORIZATION OF FOUL-SMELLING EFFLUENTS FROM PULP MILLS, Bumazh. Prom. 40 (17), 122-6, (1965).

In connection with the construction of new large kraft mills, the problem of purification of effluents from S cpds. became urgent (at present, most mills simply discharge such effluents into the rivers, causing considerable pollution and damage to the fishing ind.). A study made at the Segezha kraft mill showed that during aeration of S-contg. effluents, two processes take place, viz. the desorption of gases from soln., and oxidn. of S cpds. by the O of the air. The desorption process is based on mass transfer, and the rate of transfer is detd. by the equil. conditions, and is proportional to the degree by which the system is shifted from the equil., i.e., to the difference between the actual and the equil. concn., this difference being the "driving force" of the mass transfer process. In the equation $M = KF\Delta C$ (where M is the amt. of substance transferred from one phase into the other, F is the surface area of contact of phases, K is the mass transfer coeff.), the driving force ΔC can be expressed as a function of the initial and final equil. concns. of a given substance and of the initial and final actual concns., and hence can be calcd. and used for computing the aeration equipment. The equil. conditions of the S cpds. were studied in digester relief condensate (the aq. phase after removal of turpentine), and in the first and second stage condensates from black liquor evapn., by sep. detns. of partial vapor pressures of each component at temps. from 25 to 85°C. From the exptl. data empirical formulas were obtained expressing the partial pressures at equil. for hydrogen sulfide, MeSH, methyl sulfide, and methyl disulfide as functions of the concn. in the liquid phase and temp.

Landry, J. E., THE EFFECT OF A SECOND ORDER CHEMICAL REACTION ON THE ABSORPTION OF METHYL MERCAPTAN IN A LAMINAR LIQUID JET, Ph.D. Thesis, Louisana State Univ., 1966 (188 pages).

The laminar liquid jet was used in obtaining basic data on abosrption of MeSH in an aq. NaOH soln. because its unique fluid dynamic and operating characs. permit the use of the penetration theory for the description of the process. These data are needed for air pollution control in the paper ind. The diffusion coeffs. of CO_2, SO_2, and MeSH in water at 25°C. were measured. The gas absorption rates in the liquid jet follow the penetration theory results over the studied contact time range of 2.5 to 30 milliseconds. Absorption data for MeSH in aq. solns. of NaOH were correlated to penetration theory values for an infinitely fast irreversible reaction. The diffusion of the OH ion determines the effect on the mass transfer rate. The reaction of the dissolved MeSH with the OH ions is a very fast second order irreversible reaction. The kinetics of this reaction were inferred by extension of the penetration theory values in the parametric range studied. The absorption of dil. gas solns. of MeSH in aq. NaOH contacted in a packed absorber was predited by a method of caln. based on the penetration theory. Knowing the reaction kinetics and the phys. absorption consts., the height of chemical absorbers can be calcd.

Feuerstein, D. L., A STUDY OF MALODOROUS PRODUCTS FROM THERMAL DECOMPOSITION OF KRAFT BLACK LIQUOR, Ph.D. Thesis, University of California, Berkely, 1966.

Lab. app., procedures, and anal. methods were devd. to study the thermal decpn. of kraft black liquor. Emphasis was placed on pyrolysis in the absence of atm. O within the temp. range 400-970°C. Twenty individual unidentified S cpds. in addn. to those commonly reported as being present in recovery furnace stack gases, were isolated from the condensable pyrolytic gases. Detectable noncondensible constituents in the pyrolytic gases included H, CH_4, C_2H_6, acetylene, H_2S, Me_2S, Me_2S_2, Co and CO_2. A minimum of 20% by wt. of the total S was contained in the solid phases (residue) at 700°. This increased to nearly 40% at 970. The decreasing rate of S increase in the residue indicated that less than half of the total S would be contained in the solid phase at temps. approaching 1500°. A process is hypothesized to replace the recovery furnace and direct contact evaporator and eliminate the need for an oxidn. tower. This process should significantly reduce the malodorous gaseous emissions from the overall chem. and heat recovery system while providing a more controllable operation.

Douglass, I. B., and Price, L., STUDY OF METHYL MERCAPTAN AND DIMETHYL SULFIDE FORMATION IN KRAFT PULPING, TAPPI 49 (8), 335-42, (Aug., 1966).

The formation of MeSH (I) and methyl sulfide (II) in kraft pulping was studied to determine the influence of wood sp., cooking temp., sulfidity and cooking time. Digestions were carried out on a semimicro scale, using 1.0 g. of wood and 4.0 ml. of cooking liquor in a 7.5 ml. stainless steel digester. Four woods (spruce, loblolly pine, red maple, and paper birch) were digested at 150, 160, 170, and 180° C. for 1, 2, 3, and 4 hr. at 14.7, 22.2, and 30.5% sulfidities. After each cook, the digester contents were acidified to liberate (I), and the amts. of org. S cpds. formed were detd. by gas-liquid chromat. Under comparable conditions, hardwoods produced more (I) and (II) than did softwoods. Cooks carried out at lower temps. and for shorter times produced more (I) and (II), whereas cooking at higher temps, and for longer periods, esp. at high sulfidity, produced much more (II) than (I). Curves prepd. from the data clearly demonstrate that (I) is the primary prod. and is consumed in the formation of (II). Extrapolation of results obtained on this semimicro scale agree well with results reported from mill and pilot-plant studies.

Stanik, V., Polak, M., and Wolf, J., MECHANISM OF DIMETHYL SULFIDE FORMATION FROM KRAFT BLACK LIQUOR, Sb. Vyskum, Prac. Odboru Celulozy Papiera No. 11, 185-200, (1966).

The amt. of S-cpds. (MeSH, dimethyl sulfide, and dimethyl disulfide) in black liquor increases during concn. to a dryness of 50-60% and subsequent trmt. with Na sulfide at 220-300 C. It is gen. agreed that dimethyl sulfide (DMS) is formed in two stages. In the first, NaSH present in the liquor demethylates lignin with the formation of MeSH. The latter, or MeSNa, demethylates further portions of lignin yielding DMS. In a study of the mechanism of DMS formation, the possibility was investigated of its originating from MeSH. When heated 1 hr. at 260°C., MeSH was converted into DMS to the extent of 45%. Under similar conditions, MeSNa conversion into DMS was 68.4%. Considering that in the prodn. of DMS from black liquor there is an equil. between MeSH in the vapor phase and MeSNa in soln., it can be concluded that DMS is formed both in soln. and in the vapor phase. To study the reaction of NaOH with the Me groups of lignin, two series of expts. were conducted with black liquor. In the first, 1000 ml. liquor sample contg. 38.1 g. NaOH was heated 2 hrs. at 20°C. The yield of DMS was 73.74% of theoretical. In the second series, a similar sample contg. 69.9 g. NaOH was heated under the same conditions. The yield of DMS was 36.87%. The lower yield in the second series can be explained by more extensive demethylation of lignin with the formation of MeOH which, as exptl. demonstrated, has a low reactivity. When MeOH was heated with hydrogen sulfide or Na sulfide the yield of DMS was very low. Consequently, the reaction of NaOH with lignin can be regarded as secondary in the formation of DMS. From the pract. viewpoint, the concn. of NaOH in the prepn. of DMS from black liquor should be as low as possible, i.e., just sufficient to maintain the viscy. of the soln. at a level compatible with the reaction. 12 ref.

McKean, W. T., Jr., Hrutfiord, B.F., Sarkanen, K. V., Price, L., and Douglass, I. B., EFFECT OF KRAFT PULPING CONDITIONS ON FORMATION OF METHYL MERCAPTAN AND DIMETHYL SULFIDE, TAPPI 50 (8), 400-405, (Aug., 1967).

Rev. of available data on the formation of MeSH and DMS in kraft pulping allows estn. of the kinetic characs. of these reactions for softwoods. The summative rate of MeSH plus DMS formation is proportional to the initial hydrosulfide (HS) concn. in accordance with an S_n2 mechanism. The formation of DMS from MeSH and lignin MeO groups appears to be subject to some unusual catalytic effects. Larger amts. of MeSH and DMS are produced from hardwoods than from softwoods, because of a rapid initial demethylation of some labile MeO groups. In softwood cooks the formation of DMS can be reduced by short high-temp. cooks, while the temp. effect on MeSH formation is rather insignificant. More effective redn. of odor formation is possible by lowering the sulfidity and by minimizing black liquor recycling. 23 ref.

Feuerstein, D. L., Thomas, J. F., and Brink, D. L., MALODOROUS PRODUCTS FROM COMBUSTION OF BLACK LIQUOR: (1) PYROLYSIS AND COMBUSTION ASPECTS, (2) ANALYTICAL ASPECTS, TAPPI 50 (6), 258-62, 276-85, (June, 1967).

Undersirable side-effect malodors customarily assocd, with the kraft process may originate at 6 major points in the total system comprising digestion, inorg. chem. and heat recovery, and org. waste disposal. The recovery furnace is the major source of malodorous air pollution, fld. by evaporators, digester, lime kiln, oxidn. tower, and dissolving tank. In this study, the recovery furnace operation was assumed to include distn., sublimation, pyrolisis, auto-oxidn., stoichimetric combustion, and quenching. Single charges of spent reaction liquors were carried sequentially through these various steps in the lab. under controlled conditions, and all prods. were quant. collected and anald., thus considering the simult. individual processes in a furnace from the air-pollution standpoint. Results pointed to several unique control possibilities. Combustion techniques and sample collection are described in some detail. The gaseous and liquid produs. isolated from pyrolyzates of black liquor were anald. quant. by gas-liquid chromat. and qual. by flame ionization. More than 60 components were detected in the pyrolysis liquid, of which at least 32 were also present in the gas phases despite thorough condensation at 0°C. Detn. of S was based on microcoulometric titration using a newly devd. app. which detected H_2S, MeSH, Me_2S, Me_2S_2, and at least 19 addnl. tentatively identified or unidentified S cpds. of which 17 were detd. quant. Low-boiling org. and inorg. cpds. in the gas phase were conductivity measurements. Quant. detns. were made of H, O, N, CO, CO_2, CH_4, C_2H_6, and acetylene, whereas H_2S, MeSH, and 5 unidentified components could be distinguished qual. The S in pyrolysis residues was detd. by wet combustion. Within the exptl error, total S of all prods, equalled the total content of the original black liquor, and total S of pyrolysis prods. (excl. the residue) accounted for 70% of the black liquor S. Changes in cpn. of prods. with changes in pyrolysis (combustion) conditions indicated that increased emphasis should be placed on the overall combustion process to further reduce malodorous emissions. 32 refs.

A. C. Harkness and Murray, F. E., REACTION BETWEEN METHYL SULFIDE AND OXYGEN IN A STATIC SYSTEM, Atmos. Environ. 1 (4), 491-7, (1967).

Me_2S and O react explosively at temps. as low as 210. At 195°, the nonexplosive reaction has an initiation stage and a main stage. The rate of the main stage detd. from pressure-time curves is linearly dependent on initial O pressure, but substantially independent of initial Me_2S pressure. The extent of the initiation stage is reduced by increase in the O pressure. The chief oxidn. products are SO_2 and CO. Even with an excess of O not all the Me_2S reacts.

Hales, J. M., AN INVESTIGATION OF THE REACTION BETWEEN HYDROGEN SULFIDE AND OZONE IN A LAMINAR-FLOW REACTOR, Ph.D. Thesis, University of Michigan, 1968 (160 pages).

Exptl. data were obtained from 2 tubular laminar-flow reactors of varying dimensions concerning the kinetics of the reaction between hydrogen sulfide and ozone. Based on the data, a math. expression was devd. giving the rate of sulfur dioxide generation in the absence of light. Comparison of the data from the 2 reactors indicates that the reaction is almost totally homogeneous with the tubular laminar flow reaction rates. The study is related primarily to air pollution research, incl. work in the pulp and paper ind. 99 refs.

McKean, W. T., Jr., KINETICS OF METHYL MERCAPTAN AND DIMETHYL SULFIDE FORMATION DURING KRAFT PULPING, Ph.D. Thesis, University of Washington, 1968 (118 pages).

The kinetics of the demethylation of lignin during kraft pulping by hydrosulfide ion to form MeSH and dimethyl sulfide (DMS) were studied. Exptl. data were obtained using lab. microdigesters and a gas chromatograph for anal. of prods. Rate data were obtained for demethylation of wood meal by kraft liquor and by alk. solns. of MeSNa in the temp. range of 150-210 C. The results indicated that sulfide and hydrosulfide ions have approx. the same reactivity with MeO groups of lignin. Diffusion processes did not affect the reaction rates. Furthermore, the extent of irreversible hydrosulfide bonding with lignin by degradation reactions was found to be very small (max. 0.4% by wt. of lignin). Larger amts. of MeSH and DMS are produced from hardwoods than from softwoods, because of rapid initial detachment of some labile MeO groups. Nonionized MeSH is ineffective in reaction with lignin MeO, but its ionized form is a strong nucleophilic demethylating agent. The summative rate of MeSH + DMS formation is proportional to the intial hydrosulfide ion and MeO concns. Furthermore, the formation of DMS is proportional to MeS (mercaptide ion) and MeO concns. These results are in accordance with a second-order nucleophilic substitution rate model for demethylation. In gen., effective redn. of odor formation is possible by using the highest pulping temp. consistent with pulp quality, by lowering the sulfidity, and by minimizing black liquor recycling. High levels of residual alkali will be particularly effective by minimizing release of MeSH and by promoting conversion of methyl mercaptide ion to less odorous DMS.

Harkness, A. C. and Kelman, B. A., SOLUBILITY OF METHYL MERCAPTAN IN WATER, TAPPI 50 (1), 13, (1967).

The soly. of MeSH in water, detd. by measuring the vol. of gas absorbed at const. pressure, was 4.90 vols./vol./atm. at 30°. The differential heat of soln. was - 6.2 kcal./mole in the temp. range 0-50°. The soly. of MeSH in other solvents at 30° was also detd. (solvent and sol. of MeSH in vol./vol./atm given): 0.05M H_2SO_4, 5.06; 1M H_2SO_4, 4.29; 0.1M $NaSCH_3$, 5.39; 1M NaCl, 3.94; 1M Na_2SO_4, 2.24. The soly. of H_2S in water at 30° was 1.86 vols./vol./atm.

Shih, T. T. C., Hrutfiord, B. F., Sarkanen, K. V., and Johanson, L. N., METHYL MERCAPTAN VAPOR-LIQUID EQUILIBRIUM IN AQUEOUS SYSTEMS AS A FUNCTION OF TEMPERATURE AND pH, TAPPI 50 (12), 634-8, (December 1967).

The vapor-liquid equil. of MeSH in buffer solns. was studied as a function of temp. and pH. Measurements were made at temps. ranging from 80-185°C. using solns. buffered to pH 7, 8, 10, 12, 13, and 14 at 25° and contg. 0.000182 to 0.0451 M of MeSH per liter. These measurements also necessitated preliminary kinetic studies of the rate of disproportionation of MeSH to H_2S and Me_2S in alk. solns. An activation energy of 22.4 kcal./g.-mole was found for the reaction in 1N NaOH soln. Small corrections to the MeSH concn. were required at high concn. levels, as a result of this reaction. Vapor pressure-temp. relationships for 0.01N MeSH soln. were formulated with the pH level as a parameter. Henry's Law was found to be valid for any particular pH and temp. Henry's Law consts., the dissocn. const., and vaporization equilibrium consts. as a function of temp. were calcd. from exptl. data. An overall math. expression relating the vapor pressure of MeSH to its concn. and to H ion concn. is given for dil. aq. solns. 11 refs.

Shih, T. T. C, Hrutfiord, B. F., Sarkanen, K. V., and Johanson, L. N., HYDROGEN SULFIDE VAPOR-LIQUID EQUILIBRIUM IN AQUEOUS SYSTEMS AS A FUNCTION OF TEMPERATURE AND pH, TAPPI 50 (12), 630-4, (December 1967).

The kraft pulping process continues to increase in importance, both in regard to no. and capacity of mills. Concurrently, requirements are becoming more stringent concerning reduced emanation of odors. Data are presented that are important to an understanding of situations in which H_2S is transferred between liquid and vapor phases. Vapor-liquid equil. relationships of H_2S in buffered systems are presented as a function of temp.

and pH (at 25°C.). Measurements were made by a potentiometric titration technique at temps. ranging from 80 to 185° and using solns. buffered to pH 2 to 13 at 25°. Concns. ranged from 0.00097 to 0.0315 M of H_2S/liter of buffered soln. If the degree of dissocn. of H_2S is taken into consideration, it is then possible to express the vapor pressure of H_2S mathematically in terms of temp., concn., and pH (at 25°) of the soln. New values of the first dissocn. const. up to 185° are presented. 20 refs.

Sakhuja, L., and Basu, S., STUDIES ON THE FIXATION OF SULFIDE SULFUR IN SULFATE BLACK LIQUOR, Indian J. Technol. 6 (5), 149-52, (May, 1968).

The possibility of stabilizing sulfide S (sodium sulfide) in the black liquor obtained in the prepn. of bamboo pulp, through its oxidn. into thiosulfate by introducing oxygen or air into the liquor, thereby preventing loss of S during the soda regeneration cycle, was investigated. The influence of different variables (temp., gas velocity, degree of turbulence and duration of the oxidn. reaction) as well as the presence of different aromatic hydroxy cpds. (phenol, phloroglucinol, pyrogallol, and hydroquinone) on the extent of stabilization achieved was studied. Max. possible conversion of sulfide to thiosulfate (89%) is achieved at 80°C. The degree of turbulence has a pronounced effect on the rate of conversion. An increase in gas velocity up to 60 ml./sec. gives a continuous increase in the rate of conversion. Hydroquinone at 0.061% concn. has a pronounced catalytic effect on the reaction. 16 ref.

Murray, F. E., and Rayner, H. B., EMISSION OF HYDROGEN SULFIDE FROM KRAFT RECOVERY FURNACES, Pulp Paper Mag. Can. 69 (5), 71-4, (March 1, 1968).

The evolution of hydrogen sulfide gas from a Combustion Eng. recovery furnace was monitored for several months, along with simult. detns. of flue gas oxygen content, rate of black liquor solids flow, and air flows (primary, secondary, and total) to the furnace. The amt. of hydrogen sulfide in flue gases from the economizer section of the boiler varied from zero to ca. 700 µg./liter. It varied with the rate of solids flow to the furnace and with the total and secondary air flow rates, but appeared indep. of the primary air flow rate. 5 ref.

Douglass, I. B., SOME CHEMICAL ASPECTS OF KRAFT ODOR CONTROL, J. APCA 18 (8), 541-5, (August 1968).

The principal sources of odor in the kraft pulping process are the digester, the direct contact evaporator, and the recovery furnace. Control of odor from the digester requires the confinement of the noncondensible gases and their destruction by chlorination, burning, or by some other means. Control or odor from the direct contact evaporator depends on efficient black liquor oxidn. The recovery furnace, which can be the most serious source of air pollution, must be operated properly within its rate capacity. The chemistry of the various control measures is discussed.

Douglass, Irwin B., and Price, Lawrence, SOURCES OF ODOR IN THE KRAFT PROCESS - 11. REACTIONS FORMING HYDROGEN SULFIDE IN THE RECOVERY FURNACE, TAPPI 51 (10), 465, (October 1968).

In the recovery furnace concentrated black liquor loses its remaining water and the residual solids then undergo pyrolysis. One may assume that the black liquor solids consist of lignin- and carbohydrate-derived organics and various inorganic sulfur-containing substances such as sodium sulfate, sodium sulfite, sodium thiosulfate, sodium sulfide, or elemental sulfur. In two series of experiments, each of the inorganic substances listed was heated at 600°C, first with soda lignin and then with glucose. In the experiments using sodium sulfate and sodium sulfite, negligible amounts of hydrogen sulfide were formed. In the experiments with elemental sulfur, sodium sulfide, and sodium thiosulfate, however, heating with soda lignin or glucose caused 30-75% of the inorganic sulfur to be converted to hydrogen sulfide. These results clearly indicate that in a recovery furnace large volumes of hydrogen sulfide are formed which, if the furnace is not operated properly, may escape to the atmosphere and be a major cause of air pollution.

Douglass, I. B., Kee, M., Weichman, R. L., and Price, L., SOURCES OF ODOR IN THE KRAFT PROCESS (III) ODOR FORMATION IN BLACK LIQUOR MULTIPLE EFFECT EVAPORATORS, TAPPI 52 (9), 1738, (September 1969).

Dilute unoxidized kraft black liquor from pulping hardwood carries into the multiple effect evaporator an appreciable amount of dissolved methyl mercaptan (0.219 g/gal or 438 g/ton pulp), but very little dimethyl sulfide. This mercaptan is evidently stripped from the liquor in the evaporation process. At the relatively low temperature to which the dilute liquor is subjected in the first evaporation stage, there is no detectable dimethyl sulfide formed and only a small amount of methyl mercaptan. In successive evaporation stages, at the higher temperatures employed, larger amounts of methyl mercaptan are formed but the total amount appears to be less than that carried into the evaporator. A partially oxidized (68%) hardwood black liquor, because it has been subjected to aeration in the oxidation tower, carries into the evaporator much less residual methyl mercaptan (0.047 g/gal or 103 g/ton pulp). During the evaporation process, there is less methyl mercaptan formed in each effect, primarily because most of the sodium sulfide originally present has been converted to sodium thiosulfate. The amount of dimethyl sulfide formed from either oxidized or unoxidized black liquor was too small to measure. A more completely oxidized (99%) sample of hardwood black liquor showed less mercaptan formation than when oxidation was less complete. Another sample of "fully oxidized" heavy black liquor from a southern mill showed still less mercaptan formation under comparable conditions.

Thomas, J. F., Jones, K. H., and Brink, D. L., A MECHANISM TO EXPLAIN THE PRODUCTION OF MALODOROUS PRODUCTS IN KRAFT RECOVERY FURNACES, TAPPI 52 (10), 1873, (October 1969)

This paper reviews some fundamentals of combustion which may offer an explanation for the origin of malodorous sulfur pollutants which originate in kraft recovery furnaces and which may indicate a method to control these malodors. The combustion can be characterized by initial endothermic reactions, which degrade the organic part of the black liquor into smaller and smaller fragments, and by the competing exothermic reactions of oxidation and recombination. The recombination reactions are responsible for the formation of the malodorous compounds. It is suggested that by separating the oxidation reactions from the endothermic and recombination reactions, a furnace effluent could be produced which would be completely odor free.

McKean, W. T., Jr., Hrutfiord, B. F., and Sarkanen, K. V., KINETICS OF METHYL MERCAPTAN AND DIMETHYL SULFIDE FORMATION IN KRAFT PULPING, TAPPI 51 (12), 564-7, (December 1968).

Earlier reaction rate studies on the formation of MeSH and DMS in kraft cooks were repeated under carefully controlled conditions. Rate consts. agreed well with earlier date, but a higher rate const. was found for DMS formation above 160°C.; the difference was traced to pH effects. The rate of DMS formation was shown to be directly proportional to mercaptide concn., whereas non-ionized MeSH does not react with lignin MeO groups. As a result, the alkali charge in kraft liquor has a definite influence on the ratio of MeSH and DMS formed in the cook. Noncondensibles escaping from the blow gases of mills which cook to alkali-exhaustion (ca.pH 10.5) are, therefore, more obnoxious than those from mills maintaining adequate residual alky. Sufficient active alkali charge is hence recommended for older installations. 10 ref.

10.7.1 RESEARCH NOT REPORTED IN THE LITERATURE

In addition to the foregoing, NCASI has identified the following categories of research or specific projects which presently are under way in the industry. Results may or may not be reported eventually in the open literature. It is not possible at this time to define the scope of work more completely nor to indicate the level of effort.

a. Examination of the relationships between meteorological conditions, atmospheric visibility, kraft mill particulate emission control, and ambient behavior and size of recovery furnace system particulates.

b. Investigation of the ambient rate of odorous sulfur compounds through use of airborne instrumentation, to determine extent of atmospheric natural self-purification capacity.

10.8 NEW PULPING PROCESSES

All of the chemical pulping processes reported in this study use sulfur in some form in the cooking liquor. This gives rise to many of the air quality problems facing the industry. The most severe problems of air quality occur in kraft pulping because of the formation of odorous sulfur compounds. Almost since the inception of the kraft process, researchers have been interested in developing a process which is economically attractive and as versatile as kraft without the odor problems. The developing of widespread interest in improving air quality has given added impetus to the search for other processes. Some old studies are being re-examined and new approaches are being proposed. A first hand report on the Holopulping Process under development at the Institue of Paper Chemistry was not available in the literature.

Sanyer, Necmi, and Laundrie, James F., FACTORS AFFECTING YIELD INCREASE AND FIBER QUALITY IN POLYSULFIDE PULPING OF LOBLOLLY PINE, OTHER SOFTWOODS, AND RED OAK, TAPPI 4 (10), 640, (October 1964).

The alkaline pulp yield from loblolly pine reaches a maximum with the addition of an increasing amount of polysulfide. With the use of 12% polysulfide sulfur, the yield of kraft pulp at 50 Kappa number is increased from 50 to 61% and the respective bleached yield of pulps at 35 Kappa number from 44.5 to 53.5%. The strength properties of polysulfide pulps are comparable with kraft except tear, which is slightly lower. Polysulfide decomposes in alkaline cooking liquor before reaching the digestion temperature by an auto-oxidation-reduction reaction which has a very high temperature coefficient. This results in a large loss of polysulfide, as well as active alkali. Therefore, the active alkali requirement increases with increasing polysulfide. The use of low digestion temperature, preimpregnation, slow rate of heating to maximum temperature, and short or thin chips increases the efficiency of polysulfide. Further improvements in cooking conditions are expected to reduce the sulfur requirements to more practical levels. Although the rate of delignification in pulping with polysulfide is considerably faster than in kraft, the increase in pulp yield was primarily due to protection of wood carbohydrates, probably through the oxidation of their reducing and groups by polysulfide and decreased peeling-off degradation in alkali. The yield of glucomannan was doubled, accounting for one-half of the pulp yield increase, and 10% increases in cellulose and xylan were responsible for the other half. The response of loblolly pine, white spruce, balsam fir, and Douglas-fir to polysulfide pulping was more or less similar. With red oak the maximum-yield was about one-half that of pine, mainly because of improved xylan retention.

Mauch, R. C., OFF-GAS ANALYSIS AND REACTION RATE STUDY IN NITRIC ACID PULPING, M. S. Thesis, University of California Berkeley, 1965 (90 pages).

Gaseous components evolved from HNO_3-wood and HNO_3-wood-O_2 reactions were identified and a quant. method for their detn. was devd. The rate of oxidn. reactions of wood substance in the presence of O was found to be const., whereas the kinetics of reactions without O appeared to fit a 2nd-order pseudoreaction mechanism. 15 ref.

Hartler, N., RECENT EXPERIENCES IN POLYSULFIDE COOKING, TAPPI 50 (3), 156-60, (March 1967).

A changeover to polysulfide pulping in a kraft mill requires the introduction of new or modified techniques. Attention must be paid to the entire system if a successful result is to be achieved. Some of the pertinent factors are considered in detail. The amt. of odorous org. S cpds. formed in polysulfide cooking is higher than in conventional kraft cooking, but this is not due to the presence of polysulfide as such; before temps. high enough for the formation of org. S cpds. are reached, the polysulfide is degraded to thiosulfate and sulfide. This build-up of sulfide is probably the cause of the higher odor level. 20 ref.

Sanyer, N., PROGRESS AND PROSPECTS OF POLYSULFIDE PULPING, TAPPI 51 (8), 48-51A, (August 1968).

Polysulfide pulping reactions are discussed in relation to the high S requirement of the process, the delignification rate, the mechanism of carbohydrate protection, and increased yield. The major obstacle to com. use of polysulfide pulping is the lack of an effective recovery system. Present kraft recovery techniques can be appl. only with major modifications, because of the high sulfidity of the smelt that would result from burning of polysulfide spent liquor. It is proposed to develop a novel recovery furnace having sep. oxidn. and redn. sections with built-in air pollution abatement features. 29 ref.

Nolan, W. J., THE PULPING OF SLASH PINE, USING ROSIN PREEXTRACTED CHIPS IN KRAFT PULPING AND UNEXTRACTED CHIPS IN PULPING WITH MIXTURES OF SODIUM SULFITE AND CARBONATE, TAPPI 52 (11), 2118, November 1969.

Slash pine chips were extracted with methyl isobutyl ketone, reducing rosin content to 0.1-0.2% of dry wood. In kraft pulping, the removal of most of the rosin had no effect on pulping rate or strength of pulps. Foaming properties of black liquor were not reduced, nor were the mercaptan and hydrogen sulfide concentrations in the black liquor. In neutral sulfite semichemical pulping, preextraction of rosin had no beneficial effect. The cooking liquor (3:1-6:1 molal ratio of SO_3 to CO_3) saponified wood rosin as well as in kraft pulping. Semichemical pulps of 52-53% yield were as high in burst, tensile, and tear strength as fully cooked, screened kraft pulps and about 10 points higher in brightness on the GE scale. Energy for fibration in a 100 hp attrition mill equipped with toothed plates, operating at 20% consistency, was less than 5 hp-days per dry ton. A total cooking time (60 min. to maximum temperature of 190 C) of 160 min was required to reach 55% yield (o.d. basis) as compared to 78 min (60 min to maximum temperature of 173 C) for kraft pulping to the same yield. Increasing the ratio of SO_3 to CO_3 resulted in more selective removal of lignin and increased the rate of pulping without impairing saponification of rosin. No objectionable odors could be detected as the neutral sulfite cooks were blown.

10.8.1 RESEARCH NOT REPORTED IN THE LITERATURE

In addition to the foregoing, NCASI has identified the following categories of research or specific projects which presently are under way in the industry. Results may or may not be reported eventually in the open literature. It is not possible at this time to define the scope of work more completely nor to indicate the level of effort.

Development of new pulping process eliminating use of sulfur compounds or substituting alkaline sulfite pulping for the kraft alkaline sulfide pulping process, avoiding generation of reduced sulfur compounds.

10.9 CONTROL SYSTEMS DEVELOPMENT

The widespread interest in improving air quality has also stimulated the development of complete systems for reduction of emissions. The odorous sulfur compounds have been the major target. Many of the systems described in this section incorporate components previously described. Much work remains to be done in this area for all pulping processes.

10.9.1 KRAFT SYSTEMS

Ignatenko, A. A., Alferova, L. A., Bondareva, T. N., Volkova, T. I., and Titova, G. A., DEODORIZATION OF EFFLUENTS FROM THE MANUFACTURE OF KRAFT PULP, Bumazh. Prom. 39 (5), 16-17, (May, 1965).

Chem. analyses were made of effluents from continuous kraft pulping in a Kamyr digester at the Mariisk mill, to det. the content of foul-smelling components. All samples tested were colorless, acidic (due to the presence of volatile org. acids) and had the charac. unpleasant odor. The contents in mg./liter, of H_2S ranged from traces to 38.8, of MeSH from traces to 60, of Me_2S from traces to 59.6 to MeOH from 10.5 to 1560, and of turpentine from 2.1 to 58.6. There was no Me_2S_2, and the content of volatile org. acids was up to 348 mg./liter. The cl absorption capacity of the samples (upon 5-30 min. contact) was 460-625 mg./liter. In studying the possible means of deodorization of the effluents, it was found that the unpleasant odor disappears flg. chlorination. The amt. of Cl need is 50-75% of the Cl absorption capacity, i.e., 0.5 g./t. pulp, on the av. Another efficient deodorization method is rectification at 78-80% C., a process which removes MeOH, and foul-smelling cpds., and reduces considerably the C.O.D. of the effluent. A system combining purification of effluents with that of crude turpentine is described. In this system, the liquid from the lower part of the distn. column (after removal of the volatile fraction) goes to condensers, and then to a Florentine flask, where it is sepd. into two layers, an aq. and a turpentine layer. The crude turpentine is collected, the aq. phase is neutd., sedimented, and re-used. The volatile fraction contg. the foul smelling cpds. is condensed and further processed for the recovery of chemicals.

Lindberg, S., COMBUSTION OF MALODOROUS GASES FROM ALKALINE PULP COOKING, in Atmospheric Emissions from Sulfate Pulping (E. R. Hendrickson, Ed.), April 1966.

This paper describes an invention to get rid of malodorous air and water pollutants by combustion of gases from the cooking in a continuous digester of alkaline pulp, especially sulfate pulp. The aim of this invention is to destroy both air and water pollutants in one single operation. The application to cintinuous cooking is demonstrated with a flow diagram.

Hrutfiord, B. F., and McCarthy, J. L., SEKOR I. - VOLATILE ORGANIC COMPOUNDS IN KRAFT PULP MILL EFFLUENT STREAMS, TAPPI 50 (2), 82-5, (February 1967).

As part of a program for devt. of a process to strip aq. effluents for kraft mill odor redn. (SEKOR), a study has been made of the volatile org. cpds. that may be steam-distd. from kraft mill effluent liquors. Some cpds. have been isolated and characd. by gas chromat. The matls. studied include an oil isolated from blow gas condensate, an aq. blow gas condensate, and several crude sulfate turpentines. Cpds. identified include hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, methanol, ethanol, acetone, methyl isobutyl ketone, α-pinene, β-pinene, Δ^3-carene, camphene, limonene, cineole, and α-terpine. A large no. of addnl. cpds. have been detected. Turpentines from a no. of sources have been anald. and compared.

Maksimov, V. F., Sokolva, O. I., PURIFICATION FROM GASES OF MALODOROUS CONDENSATES OF THE EVAPORATION PLANT, Bumazh. Prom. 41 (3), 9-10, (March, 1967).

Purification of the condensate from unoxidized black liquor evapn. is usually done in the aeration method. Plant tests showed, however, that a large fraction of gaseous S-cpds, passes from the liquid into the gaseous phase and is thus discharged into the atm. At the Segezha mill, which used white liquor of high sulfidity (32-26%), about 100 cu.m. WV-satd. gases are formed/t. pulp produced during aeration. The gases contain, on the av., in g/cu.m. 4.5 H_2S 0.5 MeSH, and 0.4 Me_2S_2. Recovery of the gaseous S-cpds. was studied in an exptl. app., consisting of a plate column into which the air-gas mixt. is fed at the top and, mounted above the column, a scrubber, in which the gaseous mixt. enters at the bottom and the scrubbing liquid (white liquor) at the top. Two types of scrubbers were tested (viz., a Rashig ring-packed column and a spray (jet) column). The white liquor used in the scrubbers contained 16-22 g./liter alkali (as Na2O) and had a temp. of 75°C. Max. purification was achieved in the Rashig ring scrubber under optimum operating conditions (a white liquor flow rate of 15 cu.m/aq.m./hr. and a packed height of 2 m.). The efficiency of H_2S removal was 96-99% that of MeSH and Me_2S_2 90-95%. The efficiency of the jet scrubber was detd. mainly by the gas flow rate at the throat of the app. and the degree of dispersion of the white liquor, but even under the most favorable conditions (gas flow rate 18.22 m./sec.), the max. purification was 95%. Moreover, the alkali concn. in the white liquor was reduced to 2-8 g./liter, as compared with a redn. to 12-14 g./liter in the case of the packed column scrubber. To completely prevent the evolution of gaseous S cpds. from white liquor flg. absorption (the liquor is recycled to the causticization room) its alkali concn. should be maintained at 25-40 g./liter.

Matteson, N. J., Johanson, L. N., and McCarthy, J. L., SEKOR II-STEAM STRIPPING OF VOLATILE ORGANIC SUBSTANCES FROM KRAFT PULP MILL EFFLUENT STREAMS, TAPPI 50 (2), 86-91, (February 1967).

A pilot-plant study has been carried out of the "SEKOR" process which comprises mainly the flg. operations: the continuous steam stripping with reflux of kraft pulp mill effluents to remove volatile org. cpds. and the collection of the resultant bottoms and overhead streams to avoid discharging effluent volatile org. cpds. into the air; the recovery of an overhead stream of water-immiscible oils; the substantial removal of volatile org. cpds. from the condensate effluents, which reduces the hazard of water pollution should the effluent be discharged into water courses; and the recovery of a bottoms streams of condensate water now purified to such a degree that often it may be reused in kraft pulp mill process operation. Expts. demonstrated that hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide were removed to a degree exceeding 95%. Operations were conducted satisfactorily using steam stripping without reflux (SEKOR-a) or with reflux (SEKOR-b). When the SEKOR-b process was used under appropriate conditions nearly all of the volatile org. cpds were collected in the water-immiscible overhead stream. 9 ref.

Maahs, H. S., Johnson, L. N., and McCarthy, J. L., SEKOR III. PRELIMINARY ENGINEERING DESIGN AND COST ESTIMATES FOR STEAM STRIPPING KRAFT PULP MILL EFFLUENTS, TAPPI 50 (6), 270-5, (June 1967).

A prelim. illus. eng. design and cost est. was conducted on the SEKOR B (refluxed column) process. As basis for these calcns., exptl. detns. were made of vapor-liquid equil. consts. for MeSH, Me_2S, and Me_2S_2 in dil. aq. solns. at 1 atm. total pressure, as well as for limonene, a-pinene, as a-terpineol-major constituents of the recovered volatile oil. All these cpds. were more volatile than water and could be steam-stripped; a-Terpineol and Me_2S_2 were the most difficult to strip. The optimum feed/steam ratio reflux rate, and no. of stages required to strip H_2S plus the above cpds. from condensates of a 400t./day kraft mill were calcd. To reduce the Me_2S_2 concn. to 1% of its feed concn. capital costs were estd. at $51,500 to treat 1,000,000 lb./day of blow and relief gas condensates. If amortized over 5 yr., the capital plus operating costs would result in a total cost of 25 cents/t. of o.d. pulp for the first 5 yr., and 13 cents/t. thereafter. If recovered crude SEKOR oils could be sold at 4 cents/lb. and hot process water is valued at 3 cents/1000 gal., the costs for trg. blow and relief gas condensates are estd. at 7 cents/t. The bases for these calcns. and designs are described, permitting similar calcns. to be made for different local mill conditions. 9 ref.

Adams, D. F., and Koope, R. K., GAS-PHASE CHLORINATION OF KRAFT PULP MILL GASES, TAPPI 51 (5), 173-5, (May 1968).

Gas-phase chlorination of gases from kraft pulp mills appears to be of limited value as a means of odor reduction. In laboratory experiments, gas samples from the recovery furnace, batch digester, multiple-effect evaporator, and lime kiln of a mill were charged with known volumes of chlorine gas and the reactions were recorded by gas chromatography. The chlorine oxidized the methyl mercaptan in the gases to dimethyl disulfide but did not change the concentrations of hydrogen sulfide or dimethyl sulfide in the samples. Complete elimination of the methyl mercaptan apparently is possible if adequate chlorine doses are added. However, the odor reduction effected in the total gaseous effluent would probably not be sufficient to justify use of this process on a plant scale.

Vedernikov, V. G., and Kaksimov, V. F., SOME PROBLEMS OF DEODORIZATION OF GASEOUS WASTES IN THE KRAFT PULP INDUSTRY, Tr. Leningrad. Tekhnol. Inst. Tsellyuloz. Bum. Prom. (13), 148-54, (1964).

In the digester room, the gaseous prods. can be effectively deodorized by absorption in the so-called "doctor's soln." obtained by dissolving 6 kg. PbO and 12.5 kg. caustic soda in a 100-fold amt. of water (Na plumbite is formed in such soln.) or in a soln. of polysulfides. Me_2S_2 and Me_2S accumulate in the doctor's soln., and can be easily sepd. In the evapn. plant, deodorization can be achieved by sepg. H_2S and MeSH formed by means of a system of heat exchangers and then by absorption in the doctor's soln. or a soln. of polysulfides. In the soda recovery plant, S-contg. gases can be trapped in a desorption scrubber equipped with an electrofilter. The suggested deodorization system with full recovery of S makes the installation of equipment for oxidn. of black liquor of doubtful value. The deodorization system is connected with Me_2S is utilized, without further processing, as a solvent and/or as a starting matl. in org. synt.

Buxton, Winslow H., and LaPointe, Markley W., CHEMICAL RECOVERY AND ODOR ABATEMENT ON A KRAFT RECOVERY FURNACE, TAPPI 48 (5), 112-13A, (May 1965).

Air pollution at Western Kraft Corp. in Albany, Oregon, has substantially reduced by establishing uniform recovery furnace control and utilizing secondary stack gas chem. recovery. Using wet gas scrubbers in conjuction with an alk. shower wash, Na ion collection efficiencies as high as 50% have been reported. H_2S recovery of 90% was obtained during extensive testing. Gen. chem. fallout on mill prop has been reduced 94%.

Jensen, G. A., Adams, D. F., and Stern, H., ABSORPTION OF HYDROGEN SULFIDE AND METHYL MERCAPTAN FROM DILUTE GAS MIXTURES, J. APCA 16 (5), 248-53, (May 1966).

The absorption of hydrogen sulfide (I) and methyl mercaptan (II) by aq. solns. of Cl, NaOH, and Cl + NaOH was studied using a 2-inch diam, absorption column packed with 1/4 inch Intalox saddles. Absorption rates were noticeably affected by chem.

reactions occuring in the aq. Cl and hydroxide media. These solns. were studied as a means of controlling S-contg. gas emission at a pH above 12 were effective absorbents for (I) removal in absorption equipment designed to handle S in suspension. The absorption of (II) in aq. Cl solns. appeared to be impractical since dimethyl disulfide was apparently the only prod. formed and was stripped from the tower by the gas stream. NaOH soln. was an effective absorbent for both (II) and (I) when hydroxide to (I) or (II) feed ratios were greater than 1 or 1.8 resp. The (II) absorption coeff. was approx. twice that for sulfide absorption.

Jafs, D., RECOVERY OF HEAT AND CHEMICALS FROM FLUE GASES USING THE WARKAUS VENTURI SYSTEM, Paperi puu 48 (6), 337-9, 341-2, (June 1966).

The constructional design and operating theory of the Warkaus Venturi scrubber devd. by T. F. Holmberg (previously known as the Imatra Venturi) are outlined. The use of this device for recovering heat and chemicals is exemplified by actual case histories in which efficiencies of 90-99% (and even as high as 99.9% for a 3-stage system) were emphasized, since it is well suited for scrubbing org. S cpds. from flue gases. 19 ref.

Russ, L., SCRUBBER RECOVERS SULFUR LOSSES, Pulp Paper 40 (27), 22-3, (July 4, 1966).

Flg. a brief rev. of work in the area of odor abatement systems for the kraft pulp mill, the design and performance characs. of the Venemark scrubber, which uses a white or weak liquor and/or caustic soln. scrubbing liquor to absorb noncondensible evaporator gases, are outlined. 7 ref.

Kiyoura, R., STUDIES ON THE REMOVAL OF SULFUR DIOXIDE FROM HOT FLUE GASES TO PREVENT AIR POLLUTION, J. APCA 16 (9), 488-9, (September 1966).

A study was made of a process, applicable in ind., for removing SO_2 from hot flue gases. The process, referred to as the Kiyoura T.I.T. [Tokyo Inst. of Techno.] process converts SO_2 in the flue gas to SO_3 in the presence of vanadian oxide at a temp. of 380-450°C. A limited amt. of WV present in the flue gas reacts with SO_3 to form H_2SO_4. Ammonia is then introduced into the gaseous mixt., which is now at a suitable temp. (220-260°C.) to form $(NH_4)_2SO_4$. The $(NH_4)_2SO_4$ aggregates produced can be removed by a dry cyclone separator. The process was tested in lab. and semi-pilot plants. A pilot plant is currently under construction. Estd. operating costs of the process are given. 2 ref.

van der Feyst, J., PULP PRODUCER HELPS DESIGN RECOVERY SYSTEM, Can. Pulp Paper Ind. 21 (4), 60, (April 1968).

The devt. of a gas scrubber with a heat recovery sect. by 2 Swedish companies (Mo och Domsjo AB, and the SF group) is briefly described. The heat recovery sect. uses a ser. of 3 nozzle bank and water collector units to heat water by spraying it into the scrubbed flue gases and recollecting it.

Murray, F. E., Oloman, C., and Risk, J. B., SELECTIVE ABSORPTION OF HYDROGEN SULFIDE FROM STACK GAS, Paper Trade J. 153 (7), 92, 94, (February 17, 1969).

A process for the selective absorption of hydrogen sulfide from gas streams containing high proportions of carbon dioxide is discussed. The process involves the absorption of H_2S into a strong solution of sodium carbonate and bicarbonate and is being designed specifically for application to the flue gas from pulp mill recovery boilers.

Russ, Lennart, INVESTIGATION OF ODOR ELIMINATION AT AB MORRUMS BRUK, MORRUM, Sevensk Papperstid 66 (15), 554-7, (August 15, 1963).

A system for the redn. of odorous cpds. formed during alk. pulping, devd. by the British Columbia Research Council, consists of an oxidn. tower through which black liquor is pumped in the same direction as a gas mixt. contg. air, uncondensed gases from the turpentine recovery, and gases from the digester blow. After leaving the oxidn. tower the mixt. is washed with Cl and dil. NaOH in a scrubber before being vented into the atm. The efficiency of the system has been investigated at AB Morrums Bruk, Morrum, Sweden. The atms. of MeSH, Me_2S, and Me_2S_2 in the gas mixt. before and after the oxidn. tower and the scrubber were detd. by gas chromat. If operated under proper conditions, the system removes more than 99% of the methyl sulfides and more than 97% of the mercaptan. The greater part of these cpds. was taken up by the black liquor in the oxidn. tower, and the rest was oxidized in the scrubber. The concns. of the odorous cpds. in the outlet from the scrubber were very low and the smell was characd. as "faint." The gas mixt. leaving the scrubber is probably immediately dild. by fresh air so that the concns. of the odorous cpds. decrease below the noticeable level. The efficiency of the oxidn. tower decreased below a certain limit. About 90% of the Na_2S in the black liquor was oxidized in the oxidn. tower. 1 ref.

Murray, F. E., HOW KRAFT PULP ODOR IS ABATED, Pulp Paper Intern 6 (2), 52-3, (February 1964).

A brief rev. is given of the use of the British Columbia Research Council system in controlling odor from the kraft pulp mill of AB Morrums Bruk, Morrum, Sweden.

Collins, T. T., Jr., NEW SYSTEMS PROPOSED FOR KRAFT MILL ODOR CONTROL AND HEAT RECOVERY, Paper Trade J. 149 (22), 54-5, (May 1965).

Using stack gas heat recovery app. as a part of an odor control system, this recent invention makes profitable a combination process for redn. of kraft pulp mill odors. Three flow diagrams show the modification of basic concepts, incl. collection and disposal systems for high and low temp. gases and condensates, central heat recovery and odor control system, and modified central heat recovery and odor control system. These are also applicable to recovery of spent neut. sulfite and medium base acid sulfite liquors alone or in conjunction with kraft mills.

Nowicki, R., and Zajac-Wierzchowska, E., STUDIES ON THE CONTROL OF ODOR IN KRAFT MILLS, Przeglad Papier 21 (6), 195-8, (June 1965).

Results are presented and discussed of the study on the possibility of redg. the amt. of foul-smelling S cpds. formed during kraft cooks, and the means to deodorize these cpds. The expts. were carried out on a pilot plant scale, under conditions resembling as much as possible the ind. process used at the mill in Jelenia Gora (this included pulping variables, the digester relief process, the digester blow-off, collection of the condensate, etc.). Under the conditions prevailing at the mill, the av. amt. of foul-smelling S cpds. formed (hydrogen sulfide, MeSH, methyl sulfide), expressed as S, is 2430 g./t. pulp. Of this amt., 87% are noncondensing S cpds., which are a direct cause of the air pollution, and a major fraction of these are evolved during digester blow-off. The amt. of S cpds. can be substantially reduced by increasing the alkali content of the cooking liquor, while an increase in the liquor sulfidity has the opposite effect. Thus, expressed in g. S per t. wood an increase of alkali concn (as NaOH) from 20 to 26%, at a sulfidity of 17% caused a redn from 390 to 124, and an increase of sulfidity (at alkali concn. of 20%) to 25%, caused an increase to 580. Expts. on the deodorization of S cpds. with Cl (using spent liquor from the chlorination tower) indicated that at stoichiometric ratios, 50% of S cpds. are oxidized. For full deodorization an excess of Cl, equal to three times the stoichiometric amt., is needed. Since the spent chlorination liquor available at the mill contains less than that amt., the problem could possibly be solved by a combination of the flg. means: redn. of the mat. of S cpds. formed by modifying the pulping parameters, lowering of the temp. of gas condensation and the introduction of an addnl. amt. of Cl for deodorization. 30 ref.

Carlson, D. A., and Gumerman, R. C., HYDROGEN SULFIDE AND METHYL MERCAPTAN REMOVALS WITH SOIL COLUMNS. (Proc. 21st Ind. Waste Conf.) Eng. Bull. Purdue Univ. 50 (2), 172-9, (May 1966).

The use of soil bacteria to remove gaseous odors from kraft pulp mills, sewage facilities, sewage trmt. plants, and other inds. appears to have excellent possibilities. Microbial populations are responsible for the odor removal; water absorption, efficiencies approaching 100% were attained for a concn. of 15 mg/liter of hydrogen sulfide and for 775 mg/liter of degrade hydrogen sulfide and methyl mercaptan in quantities of 1.86 and 2.68 liters/week/cu.ft. of soil, resp. Clay, sand, and sandy loam solid low in volatile matter were inferior in degradative ability to the artificially enriched fertile loam soil. Total bacteria counts during the test period showed an initial decrease but then increased substantially once acclimation occured. Fifteen bacteria cultures were isolated from soil degrading methyl mercaptan. These included 8 Pseudonomongs, 2 Bacilius, 2 Nocardia, and 1 each of Flavobacterium, micrococcus, Phizobium. Soils oxidg. hydrogen sulfide often contained Bacilius, Streptomyces, Thiobacilius. Specific responsibility of these bacteria for the resp. boil degradations has not as yet been established. Optimum soil depth was not established, although a depth of 3.5 ft. appears to be effective. As previously noted, soil filters have been successfully appl. in the elimination of malodorous gases emanating from anaerobic sewage in residential area lift stations and/or hog and poultry farms. Larger installations, such as kraft pulp mills, could apply the soil filter principle in conjunction with a spray irrigation for the removal of excess BOD. 8 ref.

Benjamin, M., AN EXAMPLE OF PLANNING FOR POLLUTION CONTROL IN KRAFT PULPING, J APCA 16 (3), 128-30, (March 1966).

This paper deals mainly with the planning and action taken at the Owens-Illinois Kraft Pulp and Paper Mill in Jacksonville, Florida, in an effort to reduce air pollution. Steps taken at the mill over the last several yr. are outlined. These include education and training of personnel, changes in the mfg. process or equipment, installation of new equipment for redg. pollution, attention to maintenance and control, utilization of research and devt. from all sources, and relations with the public and regulatory agencies. 5 ref.

Thomas, E., Broaddus, S., and Ramsdell, E. W., AIR POLLUTION ABATEMENT AT S. D. WARREN'S KRAFT MILL IN WESTBROOK, Me., TAPPI 50 (8), 81-3A, (August 1967).

Sources of gas emission in a kraft mill were studied, and corrective equipment was installed. A system was devd. in which digester blow gases are passed through primary and secondary deodorizing scrubbers, utilizing the chlorination stage effluent. As backup, weak hypo bleach can be added to the secondary unit. Noncondensible digester relief gases are burned in the lime kiln. Oxidn. control instrs. have been installed on the two recovery boilers to insure complete combustion. One recovery boiler stack has a Cottrell precipitator, another has a Venturi scrubber. Both recovery boilers have scrubbers on their smelt tank vents. Black liquor is presently oxidized in a Trobeck-Lundberg-Tomlinson oxidn. tower before passing to the evaporators. Chem. test are performed daily to det. the efficiency of black liquor oxidn. Periodic surveys are conducted on all suspended sources of air pollution to det. the effectiveness of this abatement program.

Lindgerg, S., HOW UDDEHOLM [AB.] DESTROYS AIR AND WATER POLLUTANTS AT THE SKOGHALL WORKS (SWEDEN), Pulp Paper Mag. Can. 69 (7), 125-30, (April 5, 1968).

The Skoghall Works, center of the Uddeholm Co.'s forest ind. operations, include sawmill, kraft and sulfite pulp mills, paper mill, and chem. plants. They are located on Lake Vanern (the largest Europ. lake outside Russia) in a well populated recreational area. Malodorous gases are destroyed by combustion, and gas mixts. excl. O are burnt in the recovery boiler. Those gases that are mixed with air on collection are eliminated in a specially designed furnace, installed as a prelim. oven to a conventional boiler. The worst water pollutants are cooking and evapn. condensates. Before being discharged into the lake, the digester condensate is freed from odiferous components by blowing with steam through a column. The evapn. condensate contg. mostly hydrogen sulfide is scrubbed by mixing with backwater from the chlorination stage of the bleach plant. The total sulfide content in the waste water has been reduced from 6 to 1 lb. of hydrogen sulfide per t. of pulp. Capital outlay has been moderate (ca. $100,000), and process operating costs are low (less than $0.02/t. of pulp), comprising largely the steam consumed in the stripping column (1.2 t./hr. equiv. to 12 cents/t. of pulp, and 3 cents/t. for the oil flame in the special furnace.

Van Donkelaar, A., AIR QUALITY CONTROL IN A BLEACHED KRAFT MILL, Pulp Paper Mag. Can 69 (18), 69-73, (September 20, 1968).

Equipment, process eng., and monitoring practices at the Samoa bleached kraft mill of Georgia-Pacific Corp. in northern Calif. are described. Emphasis is placed on measurement and attempted control of malodors (H sulfide, MeSH, and org. sulfides). It is shown that through nearly 100% black liquor oxidn. stack emissions of H sulfide can be reduced nearly to zero, while mercaptans and org. sulfides can be eliminated efficiently through incineration and/or chlorination of non-condensibles from the cooking and evapn. stages. Use of telephone lines and home monitoring systems has proved valuable. Close cooperation with regulatory agencies has brought better understanding of problems and realistic guidelines for future pollution-control effort. 10 ref.

Galeano. S. F, and Harding, SULFUR DIOXIDE REMOVAL AND RECOVERY FROM PULP MILL POWER PLANTS, J.APCA 17 (8), 536-9, (August 1967).

The redn. of SO_2 emissions has become a prime goal of air quality improvements programs. Special circumstances unique to pulp mills, i.e., on-site power plants and a demand for S cpds. in the cooking liquor, suggest that wet scrubbing for SO_2 removal from boiler flue gas might be economically feasible. The use of Na_2CO_3 soln. to scrub SO_2 from power plant flue gases was studied in a pilot plant consisting of a Venturi scrubber and a cyclone. The rel. effects of the major operating variables (temp., Na_2CO_3 concn., and the gas/liquid flow ratio) on the absorption phenomenon were detd. the economics of a full-scale unit operating at a NSSC pulp mill prodg. 150 t. of pulp daily are discussed. 17 ref.

Harding, C. I., and Galeano, S. F., USING WEAK BLACK LIQUOR FOR SULFUR DIOXIDE REMOVAL AND RECOVERY, TAPPI 51 (10), 48-51A, (October 1968).

Pulp mill air pollution problems are of 3 types: odors, particulate emissions, and SO_2 emissions from power boilers. Black liquor oxidn. is the single most effective step for odor rend. Work has been completed on a pilot scale on the devt. of a black liquor oxidn. system, with subsequent use of the liquor for SO_2 scrubbing of power plant flue gases. Results of this study, conducted at the Univ. of Fla., indicate that weak black liquor from southern kraft mills can be oxidized effectively by using kerosene for foam control. A Venturi scrubber with moderate head loss (ca. 14 in. water column) gave consistent SO_2 removals above 92%. Work of earlier investigators was confirmed, showing that ca. 80% sulfide oxidn. gave the most effective SO_2 absorption without measureable release of H_2S. Saltcake makeup is virtually eliminated. Complete oxidn. of sulfide enchanced the formation of sulfates which inhibited SO_2 removal during scrubbing. The liquor can be recirculated for multiple passage through the scrubber if the pH is kept high enough to prevent lignin pptn. the intergrated oxidn. scrubbing system can achieve net savings of ca. 30 cents/t. of A. D. pulp, excl, the benefits of reduced SO_2 emissions. 9 ref.

10.9.2 SULFITE SYSTEMS

Laberge, J. C., SULFITE MAGNESIUM OXIDE SYSTEM--SULFUR DIOXIDE ABSORPTION EFFICIENCY IMPROVEMENT, TAPPI 46 (9), 538-41, (September 1963).

In 1948, the Weyerhaeuser Co. converted its Longview, Wash., sulfite plant from the Ca to the Mg-base system and became the first com. producer of Mg-base pulp. By applg. the information acquired during this study, the atm. SO_2 losses in the exhaust gases from that plant were reduced by a factor of 20 without addnl. capital investment. The SO_2 absorption system consists of a pair of absorption trains preceded by cooling towers. Each absorption train is designed to absorb the SO_2 from the flue gas of a spent liquor recovery boiler. The towers are hand-packed with 6 X 6 inc. cross partition rings. In addition to flue gases, certain other gas streams enter the absorption system. By reapportionment of these streams, an evanl. of their effects upon overall absorption efficiency was made. From this knowledge, the controlling source of excessive SO_2 loss was traced to a makeup SO_2 gas stream. The acid recirculation system was then modified to absorb the SO_2 from that makeup stream more efficiently. 2 ref.

Lea, N. S. and Christoferson, E. A., HOW SCOTT (Paper Co., Everett, Wash.) RECOVERS SULFITE BLOWPIT GASES, Pulp Paper 39 (42), 48-9, (October 18, 1965).

The hot gas flash condenser, sulfur dioxide (I) absorption tower, and assocd. piping, pumping, and heat exchange equipment employed at the mill in the recovery of I from the gases from the 12 sulfite digester blowpits are briefly described along with the use of the recovered I in cooking liquor prepn. In addn., data are presented on the economics of the recovery system.

Volgin, B. P., Efimova, T. F., and Gofman, M. S., ABSORPTION OF SULFUR DIOXIDE BY AMMONIUM SULFITE BISULFITE SOLUTION IN A VENTURI SCRUBBER, Khim. Prom. 43 (2), 132-6, (February 1967).

The absorption of SO_2 by NH_4 sulfite bisulfite solns. was studied in a model app., the Venturi tube being made of transparent plastic for better visual control of the soln. atomization. The exptl. results are presented in a series of graphs expressing the fig. relations: The degree of absorption at various amts. of the spray liquid, as a function of SO_2 concn. in the gas; the degree of absorption at various gas flow velocities as a function of the mat. of absorbent; the resistance (to flow) of the scrubber as a function of hydraulic parameters; the degree of absorption as a function of the resistance of the scrubber; the degree of absorption as a function of power consumption at various gas flow velocities and various amts. of the absorbent; the degree of absorption as a function of the Venturi throat length at various amts. of the absorbent and flow velocities; the resistance of the scrubber as a function of the total power consumption in a multistage scrubber; and the mass transfer coeff. as a function of the hydraulic parameters of the scrubber. Equations are given, expressing the exptl. relations. The data presented are to be regarded as preliminary, as the study is to be continued in equipment of larger capacity.

Nacu, A., and Constantinescu, O., PROCESS FOR REDUCING THE POLLUTING EFFECT OF SPENT NSSC LIQUORS, Celuloza Hirtie 16 (11), 418-25, (November 1967).

Chem. recovery processes for spent Na-base neut. sulfite liquors are revd. and their principles illus. by flow charts, incl., the Zimmermann (Sterling Drug), Mead, Sivola (Combustion Eng.), [illegible], Bradley (Western Pptn.), Copeland (Carthage), and I.P.C. processes ([illegible] ref.).

CHAPTER 11

RESEARCH AND DEVELOPMENT RECOMMENDATIONS

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CHAPTER 11

RESEARCH AND DEVELOPMENT RECOMMENDATIONS

SUMMARY

The investigations undertaken during the course of this study have led to the conclusion that existing technology, plus present technology in the experimental stage, still may result in emission levels which can be unacceptable to the public in some instances. Many gaps exist in our present knowledge which need to be filled by future research.

It is felt that several major gaps in technology have been identified which will need to be filled before any further great steps in progress can be taken. Brief statements of these needed areas of research of highest priority are as follows:

1. Develop and standardize methods and instruments for monitoring emissions and ambient air.
2. Assess the effect of operating variables on emissions from the kraft pulping and recovery systems.
3. Develop and standardize organoleptic techniques for determinations of process emissions and evaluation of ambient air quality.
4. Investigate new pulping methods which eliminate the use of sulfur.
5. Define the mechanisms, with emphasis on transport processes and emission interactions, which will relate emission limitations to ambient air objectives.
6. Evaluate emissions from sources in sulfite and NSSC mills and determine operating variables which affect emissions.
7. Investigate adsorption and absorption of odorous gases and reuse of the collected material in process.
8. Determine whether TRS is an effective measure of the acceptability of odorous emissions from kraft mills or must the compounds be identified more definitively.

These brief statements of needs are defined more completely and specific projects identified.

Although not a recommendation for specific research necessary to a technology breakthrough, it is felt that the industry and government regulatory agencies would benefit from more definitive information on costs. It is suggested that an effort be made to develop and encourage the use of a system for recording maintenance and operating costs.

Any listing of research needs and priorities must be under continuous review by the industry and NAPCA.

11.1 AREAS OF NEEDED RESEARCH

Previous chapters of this report have evaluated existing control technology, relatively untried or nearly developed control technology, and research underway related to emissions control. These evaluations have led to the conclusion that existing technology plus present technology in the experimental stage, still may result in emission levels which can be unacceptable to the public in some instances. In bringing presently major sources under control many gaps appear in our knowledge. As these sources are brought under control, presently minor sources assume greater importance. The problem of identifying the most important research needs is complicated by the fact that some mills are located in remote areas and some in cities. Some mills are old and some represent fairly new installations. Many gaps exist in our present knowledge of evaluation, effects, process variables, and application of control techniques. Major research needs have been developed taking into consideration that the kraft odor problem is the most troublesome, there are more kraft mills than other types, and little is known of the emissions from sulfite and NSSC. Of course, any listing of research needs and priorities must be under continuous review by the industry and NAPCA.

It is felt that several major gaps in technology have been identified which will need to be filled before any further great steps forward can be taken. These needed areas of research of highest priority are as follows:

11.1.1 DEVELOPMENT AND STANDARDIZATION OF METHODS AND INSTRUMENTS FOR MONITORING EMISSIONS AND AMBIENT AIR

This probably is the foremost needed research effort. Reliable evaluation methods are necessary to provide more definitive information on receptor effects, establish emission standards, determine compliance with emission standards, establish ambient air standards, determine progress toward air quality objectives, establish applicability of control measures, determine efficacy of ameliorating measures, and for many other purposes.

Although much progress has been made in this direction in recent years, few methods have been standardized and there are no reliable methods available for some compounds of interest.

Specific projects are listed in Section 11.2.3.

In general, the need is to develop and/or standardize methods for both ambient and source sampling which achieve a state of greater reliability and simplicity for continuous application in the field. It is imperative, also, to promulgate a set of sampling specifications for uniform application thoughout the industry.

11.1.2 ASSESSMENT OF THE EFFECTS OF OPERATING VARIABLES ON EMISSIONS FROM THE KRAFT PULPING AND RECOVERY SYSTEMS

For many sources, in the immediate future, it is felt that control of operating variables holds the greatest promise of meeting emission limitations. It must be recognized, however, that not all of the variables will be mutually independent.

Some work has been done on units such as the recovery furnace. This work is encouraging, and serves to emphasize the need for more difinitive and extensive work on the recovery furnace as well as other unit processes.

Most applicable odor regulations probably can be met with adequate black liquor oxidation. Definitive information is lacking, however, on the various factors influencing both weak and concentrated BLO. The reversion phenomenon particularly needs explanation. Since some new systems eliminate the DC evaporator and thus do not require BLO to reduce H_2S emissions from that source, it is important to evaluate any H_2S contribution in wet-bottom precipitators using unoxidized black liquor.

Included in this area of investigation might be an evaluation of possible alternatives to the present system of furnace recovery.

Specific projects are listed in Section 11.2.1, 11.2.5, and 11.2.6.

11.1.3 DEVELOPMENT AND STANDARDIZATION OF ORGANOLEPTIC TECHNIQUES FOR DETERMINATIONS OF PROCESS EMISSIONS AND EVALUATION OF AMBIENT AIR QUALITY

In the final analysis, the human nose will be the judge of the success of odor abatement activities. The sense of smell, however, is notoriously variable due to physiological as well as external physical factors. Except in the case of trained observers, odor panels leave much to be desired.

Some work has been done on application of organoleptic techniques in Sweden but only a limited amount of work has been done in the U. S. There is little agreement on odor threshold levels, but concentrations of odorants frequently are perceptible at levels far below the detection limit by chemical methods. A better understanding is needed of the influence of physical, physiological, and psychological factors on odor perception.

Specific projects are listed in Section 11.2.6 and 11.2.9.

11.1.4 INVESTIGATION OF NEW PULPING METHODS, ESPECIALLY THOSE WHICH ELIMINATE THE USE OF SULFUR

The most positive way of eliminating problems associated with the emission of sulfur compounds is to eliminate the use of sulfur in the process of wood pulping. It must be recognized that eradication of these problems may result in the creation of others. The long-range objective of this research and development is to provide a permanent solution.

Since the advantages and versatility of the sulfate process over the soda process were recognized beginning in the late 19th century, researchers have been attempting to eliminate the odor. In addition to add-on equipment and process modifications, new pulping bases (acid, neutral, and alkaline) have been investigated. Other delignification techniques also have been tried. Several of the processes appear promising.

Other approaches such as wood chip modification prior to cooking may make possible the use of modifications of present cooking bases under conditions which will not form objectionable compounds.

Specific projects are listed in Sections 11.2.7 and 11.2.8.

11.1.5 DEFINITION OF THE MECHANISMS, WITH EMPHASIS ON TRANSPORT PROCESSES AND EMISSION INTERACTIONS, WHICH WILL RELATE EMISSION LIMITATIONS TO AMBIENT AIR OBJECTIVES

It is necessary to develop the background information and procedures by which it will be possible to formulate meaningful emission standards for chemical wood pulping installations.

Mills of the pulp industry are widely distributed throughout the U. S. in areas of varying climatic conditions. Conversions and combinations are known or believed to occur after gaseous compounds leave the source. Adsorption of odorants on particulates has been postulated to explaint the extreme transport distances reported for some mill emissions. Dilution in the atmosphere undoubtedly will play an important but quantitatively undetermined role in providing ambient air quality which will be acceptable under all conditions.

This is a unique modelling situation involving various combinations of gases and particulates. Present dispersion modelling techniques can provide only a bare foundations for the needed effort.

Some of the projects which will provide needed background will be found in Sections 11.2.1, 11.2.3, 11.2.6, and 11.2.9.

11.1.6 EVALUATION OF EMISSIONS FROM SOURCES IN SULFITE AND NSSC MILLS AND DETERMINATION OF THE OPERATING VARIABLES WHICH AFFECT EMISSIONS

The intensive work done on this project has demonstrated the paucity of information on these sources. Before definitive progress can be made in determining what reductions are required and the most appropriate ways to bring about the reductions, reliable information on emissions is essential.

Some of the work described in Section 11.2.3 must be completed and existing methods verified before progress can be made.

11.1.7 INVESTIGATION OF ADSORPTION AND ABSORPTION OF ODOROUS GASES AND REUSE OF THE COLLECTED MATERIAL IN PROCESS

For some sources, control of operating variables or modification of unit process may not reduce emissions of odorants to an acceptable level. Until processes are available which avoid the formation of odorants, destruction or add-on devices may be the only answer. To improve the economics and avoid creation of other problems, reuse may be necessary.

Specific projects which will contribute to this objective will be found in Section 11.2.1, 11.2.4, and 11.2.5.

11.1.8 DETERMINATION OF WHETHER TRS IS AN EFFECTIVE MEASURE OF THE ACCEPTABILITY OF ODOROUS EMISSIONS FROM KRAFT MILLS OR MUST THE COMPOUNDS BE IDENTIFIED MORE DEFINITIVELY

Little is known about the human perception of mixtures of odorants. The odorants may continue to react in the atmosphere so that the perceived odor is not always the same as the one emitted. The odor threshold concentration of each compound in a mixture does not vary uniformly with changes in temperature, pressure, and humidity. Further, examples have been noted of counter-action (net lowering of perceived odor in mixtures of odorants) and synergism (increase of perceived odor in mixtures of odorants). A TRS concentration where all of the sulfur is present as H_2S may be perceived differently than the same TRS concentration made up of equal parts of H_2S, RSH, RSSR, and RSR. Whether these subtleties will decrease the value of a TRS determination as a measure of acceptability needs to be determined. The alternative may be a complicated and costly alternative. The results will have an important bearing on the work proposed in Section 11.1.5.

11.2 SPECIFIC R & D PROJECTS

Section 11.1 defined eight major areas of research effort in which work is required to produce substantial progress in emissions control. This section describes specific project areas arranged in categories similar to those in Chapter 10, but keyed insofar as possible to the eight major areas.

11.2.1 EMISSION CONTROL TECHNOLOGY

The following projects are among those necessary to fulfill the objectives of Section 11.1.2.

a. Obtain more definitive information on weak and strong BLO (e.g. identification of catalytic agents, effect of pH, and effect of thiosulfate concentration on reaction rate and completion; effect of BLO on subsequent emissions from ME evaporators, DC evaporators; Venturi evaporators, and recovery furnace for hydrogen sulfide and other sulfur compounds).

b. Determine the factors which affect the "reversion" of thiosulfate to sulfides when oxidized black liquor is evaporated.

c. Investigate the contribution of hydrogen sulfide from contact between flue gases and unoxidized black liquor in wet bottom precipitators.

d. Continue studies on effect of operating variables on odorous emissions from recovery furnace.

e. Determine the effect of operating variables on emissions and gas volumes from slakers, evaporators, and smelt tank.

f. Compare emissions from batch and continuous digesters as a function of operating variables (temperature, time, sulfidity, wood species, et cetera).

g. Compare emissions from lime recovery using rotary kiln versus fludizied bed calciner. Also delineate factors which influence emissions (e.g. operating variables and form of sulfur in lime mud).

h. In general, emission data collected in the future should be related to process and operating conditions which existed at the time of the sampling.

The following projects propose investigation of possible alternatives to presently used emission control schemes which may improve effectiveness or be more economical:

i. Investigate alternatives to treat stack gases effectively and economically to remove odorous sulfur gases (e.g. alkaline liquor scrubbing, caustic liquor scrubbing, thermal oxidation, absorption and chemical oxidation).

j. Evaluate the effectiveness of injecting vent gas from the smelt tank into the flue gas duct ahead of the ID fan.

k. Investigate alternative treatment methods for control of odorous emissions from evaporators, slakers, smelt tank, and BL oxidizers.

l. Investigate feasibility of using bag filters for particulate collection on various sources.

m. Investigate alternative methods for collection and disposal of bark char (e.g., scrubbers and precipitators).

n. Determine whether odorous sulfur compounds can be destroyed in the digester before blowing.

o. Investigate application and feasibility of using brown stock washer vent gases as forced draft air supply for the recovery furnace.

The following projects are intended to provide needed information on emissions which is not presently available or evaluate effects of control techniques presently in use or proposed:

p. Evaluate the effect on the environment of converting essentially all TRS emissions to sulfur dixoide by thermal oxidation.

q. Identify and quantify particulate and gaseous emissions from "minor" sources in the kraft, sulfite, and NSSC processes. Place emphasis on odorous sulfur gases. Relate emissions to operating and process variables. (Minor sources include brown stock washers, hot wells, mud washers, waste water sumps, waste water treatment facilities, et cetera).

r. Evaluate emissions from vented and closed circuit pressure brown stock washers.

s. Evaluate the effects of scrubbing with oxidized weak black liquor on subsequent evaporation of the liquor and chemical recovery cycle.

t. Evaluate results on emissions of burning noncondensibles in a fludized bed calciner.

11.2.2 COST AND EFFECTIVENESS OF EMISSION CONTROL

The basis for selection of a particular control scheme is an evaluation of the cost and effectiveness. Better information is needed for operating and maintenance costs on existing systems and cost data should be developed for proposed techniques. This would help to evaluate the economic impact of various abatement alternatives. The following projects will aid in obtaining such information:

a. Investigate the economics of the various alternatives to maintaining the performance level of high-efficiency particulate collection systems.

b. Parts of i, k, l, m, n, and o in Section 11.2.1.

c. A more detailed look into some of the subtleties of sulfur recovery as more and more operating data are gathered on some of the proposed SO_2 recovery systems.

d. Evaluate cost-effectiveness of "multi-use" control devices (e.g.,scrubbers effective on both particulates and certain gases).

e. Encourage collection of better information on annual operating effectiveness and maintenance costs on all types of control equipment.

11.2.3 SAMPLING AND ANALYTICAL TECHNIQUES

The following projects are among the most important in fulfilling the objectives of Section 11.1.1.

a. Develop and standardize analytical methods for malodorous sulfur compounds at ambient air concentrations (both manual and instrumental methods).

b. Conduct extensive intercomparisons of instrumental and wet chemical methods at a number of sites ranging from a simple situation where a pulp mill represents the primary source of pollutants to a complex situation where other types of pollutants also exist.

c. Conduct extensive intercomparisons of available analytical methods on a variety of mill and synthetic sources to establish the reliability and inconsistencies of each.

d. Examine possible changes which may take place in flue gas samples as they pass through sample lines of varying lengths, materials of construction, and temperature.

e. Verify the separation of sulfur compounds in the presence of other non-sulfur compounds by preselective filtration.

f. Evaluate sophisticated gas chromatographic instrumenation under mill conditions.

g. Promulgate a set of sampling specifications for uniform application throughout the industry.

h. Encourage increased use of continuous TRS monitors on a variety of sources in the mills (e.g., recovery furnace, lime kiln, smelt tank, evaporators, blow tank, and digesters), and determine limitations.

i. Encourage a series of regional workshops regarding application of TRS monitors and exchange of constructive information by working personnel.

j. Improve reliability of TRS instrumentation and required ancillary equipment for monitoring and process control.

k. Extend the development of the basic principle of newer detectors such as the Whittaker electrochemical cells to units which will exhibit selectivity for the odorous compounds of interest.

The following projects are among those necessary to fulfill the objectives of Section 11.1.6:

l. Develop analytical techniques applicable to sulfite and NSSC processes particularly where these sources are near other known sources.

m. Develop instrumental method for sulfuric acid aerosol in the ambient air.

11.2.4 CONTROL EQUIPMENT DEVELOPMENT

In the immediate future, dependence will have to be placed, in many locations, on add-on control devices. The following projects are intended to improve the reliability and application of such devices:

a. Development activities to improve reliability and lower operating maintenance costs of control devices.

b. Develop and assess scrubber or other systems for removal of SO_2 and TRS compounds of interest simultaneously.

11.2.5 PROCESS CHANGES

The following projects are among those necessary to fulfill the objectives of Section 11.1.2:

a. Evaluate the effectiveness of new recovery boiler designs which eliminate direct contact between the flue gases and the black liquor, and investigate the effect of operating variables on all gaseous and particulate emissions.

b. Evaluate the impact of high black liquor solids (62 - 65 percent) requirements on emissions from ME evaporators.

c. Investigate possible alternatives to furnace recovery of valuable costituents in spent liquors.

d. Investigate designs for improving oxidation of the black liquor in the diffusion washer zone of continuous digester systems.

e. Study various stripping operations to determine the effectiveness for removal of odorous compounds from liquid streams.

11.2.6 CHEMISTRY OF POLLUTANT FORMATION OR INTERACTIONS

The following projects are among those necessary to fulfill the objectives of Sections 11.1.2, 11.1.3, and 11.1.5.

a. Obtain more complete knowledge of the reaction between oxidized and unoxidized black liquor with flue gases.

b. Investigate the conditions which control the generation of odorous sulfur compounds in the recovery furnace itself.

c. Elucidate the role of adsorption of odorous sulfur gases on concomitant particulates on human odor perception and response.

d. Also item c with respect to the validity of reported concentrations obtained when ambient air is either sampled through filters or passed directly into the collector or impinger.

e. Investigate transformation of kraft emissions during transport and diffusion in the ambient air.

f. Determine the chemistry of oxidation of RSH, RSR, RSSR, H_2S, and $S^=$.

g. Chemical characterization of non-sulfur compounds in recovery furnace emission.

11.2.7 NEW PULPING PROCESSES

The following projects are among those necessary to fulfill the objectives of Section 11.1.4:

a. Intensify investigations into Holopulping.

b. Continue efforts toward development of other sulfur-free pulping systems.

11.2.8 CONTROL SYSTEM DEVELOPMENT

Several new developments have occurred in recent years which promise reduced emissions. These have not been combined into workable systems as yet. To satisfy some of the objectives of Section 11.1.4 evaluations should be made of emissions and economics of various combinations of the following:

a. Solvent extraction of chips
b. Increased permeability of chips
c. High-yield soda cook
d. Alkaline sulfite cook
e. Vapor-phase kraft cook
f. Oxygen/alkali bleaching
g. Standard recovery
h. Berkeley VC recovery

11.2.9 OTHER

The following projects are among those necessary to fulfill the objectives of Sections 11.1.3 and 11.1.5:

a. Develop and standardize methodology for evaluating human response to odor annoyances.

b. Intensify research into receptor effects (physical, biological, and aesthetic) of chemical pulp mill emissions.

CHAPTER 12

CURRENT INDUSTRY INVESTMENT AND OPERATING COSTS

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CHAPTER 12

CURRENT INDUSTRY INVESTMENT AND OPERATING COSTS

SUMMARY

Past estimates of the expenditures made by the wood pulping industry for air quality control have indicated that substantial sums are involved, but the numbers vary widely. Because of congressional interest in the impact of the federal air quality control program on all aspects of the economy, cost figures for the wood pulping industry would have to be obtained on a rational basis. Using the latest available data, estimates were made of the replacement cost and the annual operating cost of air quality control equipment in present operation in the industry.

Sophisticated engineering cost estimates were prepared in three categories: (1) Total Installed Cost (for replacement), (2) Total Annual Cost, and (3) Net Annual Cost (which reflects a credit for recovered materials). Estimates were prepared for a variety of controls on a number of sources. It should be noted that the cost analyses in this chapter are based on prices of chemicals and equipment as of January 1969. As these prices change the whole balance could change.

Total Installed Cost for kraft was in excess of $166 million and for sulfite about $900,000. Total Annual Cost for kraft was about $24 million and Net Annual Cost about the same. Net Annual Costs for sulfite indicated a slight net return.

12.1 INTRODUCTION

Over the past 5 to 10 years a number of estimates has been made of expenditures by the wood pulping industry for air quality control. The estimates have indicated that substantial sums of money are involved, but the numbers vary widely. In attempting to update the data and provide a foundation for projections into the future it was discovered that the basis of most of the projections was obscure. Even where fairly good coverage of the industry was obtained by questionnaire, the cost items included in the replies varied from company to company and even mill to mill.

Since Congress is vitally interested in the economic impact of the federal air quality control program, now and in the future, it was determined that cost figures would have to be obtained on a rational basis.

There are several cost categories which must be identified and assigned a cost before a total cost estimate can be prepared. Tangible items of cost are identified in this chapter. There are, however, intangible cost categories such as research and development, engineering, and air quality monitoring which are an integral part of the environmental protection picture, but for which cost estimates are difficult to make.

Activities, such as research and development, engineering, and air quality monitoring contribute extensively to the total bank of knowledge on emission sources, control techniques, and the effects of emissions; but the costs for such activities have not been estimated for this report.

12.1.1 PURPOSE OF THIS CHAPTER

The purpose of this chapter is to assess the cost of emissions control for the wood pulping industry. Specifically it is desired to determine the replacement cost and annual operating cost of air quality control equipment in present operation in the industry.

It should be noted that the cost analyses in this chapter are based on prices of chemicals and equipment as of January 1969. As these prices change the whole balance could change.

12.1.2 EVALUATION OF METHODS FOR DETERMINING COSTS

There are two methods by which the desired result could be achieved. These are a direct survey of the industry or an engineering cost estimate for specific types of equipment coupled with an inventory of the number of such items installed today. The latter alternate was chosen for this study.

Contacts with the industry revealed that accounting procedures varied widely within the industry. Some companies charge part of the cost for a particular system to air quality control and part to process, while others may charge the entire cost to either one or the other. Maintenance charges are not always charged to a specific piece of equipment, but perhaps to a group of equipment items or to a section of the plant. For these reasons, it would be difficult, if not impossible, to determine the required costs on any kind of a common basis. Therefore, the second alternate, that of an engineering cost estimate, was chosen.

12.1.3 SPECIFIC PLAN FOR ASSESSMENT OF COSTS

The plan chosen consisted of four steps:

1. Determining what types of equipment and/or systems for air quality control are now installed in the pulp industry.

2. Develop cost data by means of an engineering estimate for those items.

3. Determine the actual number of each such item currently installed in the industry.

4. Using 2 and 3 above, calculate the replacement cost for air quality control systems.

Steps 1 and 2 above were covered in Chapter 5 of this report. Step 3, for the kraft industry, was accomplished through a study of the NCASI-NAPCA kraft pulp industry questionnaires. Forty-four of the questionnaires were examined.

These forty-four questionnaires, covering 38 percent of the 116 known kraft mills, account for a daily air dried pulp capacity of 40,319 tons or 46 percent of the total of 87,808 tons per day. The data obtained from these questionnaires were extrapolated to the total industry, modified by in-house knowledge and discussions with NCASI. Items covered in this survey included type of digesters; yield; treatment of noncondensible gases; black liquor oxidation; recovery boilers; lime kilns; and types of controls on recovery boilers, smelt dissolving tanks and lime kilns.

The same type of tablulation was made based on data from Post's Pulp and Paper Directory, 1969 edition, for comparison. These data, extrapolated in the same manner gave essentially the same results. The extrapolated totals on which the calculations were made are shown in Table 12-1.

Questionnaire data for the sulfite and NSSC processes were not available to this study team. Therefore, only gross estimates can be made as to the number of specific control schemes which are utilized.

For sulfite mills only three types of controls have been described in Chapter 5. These are (1) blowpit-condenser with cyclone and packed tower, (2) blowpit with packed tower, and (3) packed tower added to the acid tower. It is estimated that only 2 mills utilize the first control method, about 10 mills utilize the 2nd method, and 22 mills utilize the 3rd method.

For NSSC mills, the only specific control device, in addition to those used for sulfite, is a scrubber serving the Copeland reactor. Only 2 or 3 mills are expected to employ this scheme.

TABLE 12-1

AIR QUALITY CONTROL IN THE WOOD PULPING INDUSTRY
EQUIPMENT AND PROCESSES PRESENTLY EMPLOYED FOR KRAFT

Item	Number Of Mills	Percent Of Total
Digesters:		
Batch (only)	77	66.4
Continuous (only)	13	11.2
Batch & Continuous	26	22.4
	116	100.0
High Yield (≥48 percent)	34	29.3
Low Yield (≤48 percent)	82	70.7
	116	100.0
Noncondensible Gases:		
Vented	85	73.3
Incinerated in lime kilns	13	11.2
Scrubbers (cyclonic, packed towers, etc.)	16	13.8
Catalytic Oxidation Units	2	1.7
	116	100.0
Black Liquor Oxidation Units:		
Weak	21	18.1
Strong	21	18.1
None	74	63.8
	116	100.0

TABLE 12-1 (Cont'd)

Item	Number Of Units	Percent Of Total
Recovery Boilers:		
Units with Electrostatic Precipitators	244	86.2
Units with Venturi Evap/Scrubbers	39	13.8
Total Number of Recovery Boilers	283	100.0
Actual Number of Precipitators	196	
Secondary Scrubbers on Precipitators	11	5.6
Secondary Scrubbers on Venturi Evap/Scrubbers	7	17.9
Dissolving Tanks:		
Units with no Control	96	33.9
Units with Mesh Pads	156	55.1
Units with Packed Towers	3	1.1
Units with Cyclonic Scrubbers	28	9.9
	283	100.0
Lime Kilns:		
Rotary Kilns	189	99.0
Fluid Bed Kilns	2	1.0
	191	100.0
Scrubbers:		
Units with Dust Chamber or Similar	32	16.8
Units with Peabody or Similar	102	53.4
Units with Cyclonic Scrubbers	11	5.8
Units with Venturi Scrubbers	44	23.0
Units with no Scrubbers	2	1.0
	191	100.0
Total Number of Power Boilers	347	

12.2 INCREMENTAL COST CATEGORIES

Three broad classes of costs are used to define the cost of air quality control devices presently installed in the pulp industry. These are: (1) Total Installed Cost, (2) Total Annual Cost and (3) Net Annual Cost.

Obviously, there are several categories within each of the three broad classes.

There are six cost categories which must be considered in arriving at Total Installed Cost. The first item of cost is that of the control device itself, purchased equipment. Other cost items are equipment erection, equipment foundation and building, process instrumentation and piping, power wiring and lighting, and indirect costs which include contingency, engineering, construction supervision, general construction overhead, spare parts, and sales tax. In turn, each of these cost categories is influenced by several variables which depend on specific circumstances; some can only be evaluated on a mill-by-mill basis.

Equipment costs are dependent upon collection efficiency, size, and material of construction. Equipment erection costs are dependent on labor rates. The amount of labor involved is obviously influenced by the material of construction of the control device, size, site conditions, as well as the physical location of the control device (on the ground or on top of a building).

Building costs are controlled by local building codes and by labor rates and are dictated in the first place by climatic conditions. Foundation costs are affected by soil conditions, labor rates, and material costs. Process instrumentation and piping, and power wiring and lighting costs are determined by labor rates and by material costs.

Total Annual Cost includes charges for labor (including overhead), maintenance, utilities (electricity or steam, fuels, water, air and others), materials and chemicals, waste water disposal facilities and/or methods, taxes and insurance, depreciation and interest, and administrative costs.

Net Annual Cost is identical to Total Annual Cost, except that credit has been allowed for recovery of heat and/or chemicals. More details concerning the method of calculation used for these cost categories may be found in Chapter 5.

12.2.1 TOTAL INSTALLED COST

The data contained in Table 12-1 were used along with cost data from Chapter 5 to determine the total installed cost which would have to be expended by the kraft industry to replace existing air quality control systems. To illustrate the method used, an example using electrostatic precipitators installed following recovery boilers is shown below:

Number of recovery boilers = 283

Total daily capacity = 87,808 A.D. Tons

Average tonnage per recovery boiler = 87,808 ÷ 283 = 310 TPD

Number of recovery boilers with precipitators = 244

Actual number of precipitators = 196

Average number of precipitators per recovery boiler = 196 ÷ 244 = 0.804

Average tonnage per precipitator = 310 ÷ 0.804 = 386 TPD

Gas flow at precipitator per A.D. TPD = 350 ACFM

Average gas flow per precipitator = 386 x 350 = 135,000 ACFM

Assumed average precipitator = Tile, wet bottom, 95 percent efficiency

Cost per unit = $540,000

Total installed cost for the industry = 196 x 540,000 = $105,840,000

This figure represents the total cost to replace the 196 electrostatic precipitators. Perhaps 10 percent of this value ($10,580,000) could be directly chargeable to air quality control. Costs for other units were calculated in a similar manner and are tabulated in Table 12-2. All costs are on a January 1, 1969, basis.

Data presented in Chapter 2 suggest that the average size of sulfite and NSSC mills is about 250 TPD. For purposes of estimating the replacement cost of current control equipment we have taken costs from Chapter 5 for the 200 TPD mill.

With this assumption, one estimates that the replacement cost of control equipment installed at sulfite mills is approximately three million dollars. Data are not available to allow an estimate of the replacement cost of control devices installed at NSSC mills to be made.

The costs estimated above do not include an estimate for costs of controls on power boilers associated with sulfite and NSSC. No accurate count is available to suggest the number of such boilers which might exist.

12.2.2 TOTAL ANNUAL COSTS

Total annual costs were developed in a manner similar to the method used to determine total installed costs in the previous section. Table 12-3 lists this cost for the same items in Table 12-2.

TABLE 12-2

AIR QUALITY CONTROL IN THE WOOD PULPING INDUSTRY TOTAL INSTALLED COST FOR EQUIPMENT FOR KRAFT

Item	Total Installed Cost
Noncondensible Gas Treatment	
Lime Kiln Incineration	$ 400,000
Catalytic Oxidation	300,000
Scrubbers	500,000
Black Liquor Oxidation Units	
Weak Black Liquor Oxidation	5,400,000
Concentrated Black Liquor Oxidation	5,800,000
Recovery Boilers	
Electrostatic Precipitators (196 units)	105,800,000*
Secondary Scrubbers on Electrostatic Precipitators	1,600,000
Secondary Scrubbers on Venturis	2,000,000
Dissolving Tank Vents	
Mesh Pads	2,000,000
Packed Towers	100,000
Cyclonic Scrubbers	1,100,000
Lime Kiln Scrubbers	
Venturi Scrubbers	4,000,000
Peabody and Similar Types	7,800,000
Cyclonic Scrubbers	500,000
Power Boiler Mechanical Collectors	29,000,000
	$166,800,000

*This figure represents the total cost to replace the 196 known electrostatic precipitators. Perhaps 10 percent of this value ($10,580,000) could be directly chargeable to air quality control.

T A B L E 12-3

AIR QUALITY CONTROL IN THE WOOD PULPING INDUSTRY TOTAL ANNUAL COST FOR EQUIPMENT FOR KRAFT

Item	Total Annual Cost
Noncondensible Gas Treatment	
Lime Kiln Incineration	400,000
Catalytic Oxidation	100,000
Scrubbers	200,000
Black Liquor Oxidation Units	
Weak BLO	1,800,000
Conc. BLO	2,500,000
Recovery Boilers	
Electrostatic Precipitators (196 units)	. . . . .*
Secondary Scrubbers on Elect. Ppts.	700,000
Secondary Scrubbers on Venturis	800,000
Dissolving Tank Vents	
Mesh Pads	600,000
Packed Towers	35,000
Cyclonic Scrubbers	300,000
Lime Kiln Scrubbers	
Venturi Scrubbers	1,600,000
Peabody & Similar Types	3,000,000
Cyclonic Scrubbers	100,000
Power Boiler Mechanical Collectors	12,000,000
	$24,135,000

*Total Annual Cost for the 196 precipitators was estimated at $28,100,000. It is not possible, however, to assess the true portion of this cost which could be directly chargeable to air quality control.

Total annual costs for control equipment in sulfite mills is estimated as:

1. Blowpit: condenser with cyclone and packed tower	--	$262,000
2. Blowpit: packed tower	--	$580,000
3. Packed tower added to acid tower	--	$ 57,200
Total	--	$899,200

The above estimates do not include costs for controls on power boilers associated with sulfite or NSSC mills because no accurate count is available to suggest the number of such boilers which might exist.

It was originally planned to include an extensive table of maintenance costs, based on data from actual operating mills, for all types of installed air quality control systems. However, it became readily obvious that this could not be done since the majority of mills do not have such charges documented by specific equipment items. The limited amount of information which was collected is presented in Table 12-4 which summarizes the costs in cents per ton of air dried pulp production. Each value shown represents a specific piece of equipment. The data include varying sizes of equipment and varying ages of equipment.

TABLE 12-4

CONTROL EQUIPMENT MAINTENANCE COST

Item	Specific Values Cents per ton of pulp produced
Electrostatic Precipitators	29.6, 5.4, 3.9, 2.9, 2.5, 2.3, 2.3
Recovery Boiler Fans	3.2, 2.0, 1.0, 0.9, 0.5, 0.4
Scrubbers (All Types)	2.8, 2.4, 2.0, 1.0, 0.5
BLO Systems	2.8, 1.0, 0.5
Bark Boilers (Ash Collecting Equip.)	1.8, 0.7
Bark Boilers (Fans)	1.7, 0.5

Figure 12-1 attempts to portray the maintenance cost data for precipitators as influenced by process size. This figure shows that cost per ton for maintenance generally decreases as process size increases. Built into this curve, however, is the fundamental fact that the smaller sizes (which have the highest maintenance) are also the older units. Undoubtedly, it is a combination of both size and age which influences maintenance costs.

Table 12-5 represents the output from another approach toward establishing annual maintenance charges for existing emission control equipment. Engineering estimates of maintenance costs, used in Chapter 5 as part of the annual operating cost, were coupled with data in Table 12-1 to give the results shown in Table 12-5. This estimate totals nearly three million dollars annually.

12.2.3 NET ANNUAL COSTS

Net annual cost is identical to total annual cost except that credit has been allowed for the value of the recovered chemicals. For the kraft process, the only equipment items to which this has been applied are the electrostatic precipitators, secondary scrubbers installed subsequent to electrostatic precipitators, venturi evaporator/scrubbers, and lime kiln scrubbers. With the exception of the precipitators, the cost data from Chapter 5 were used directly.

Table 12-6 lists the net annual cost to the kraft industry for operating existing air quality control equipment and totals just over $23 million.

In sulfite mills, cost estimates for the blowpit: condenser with packed tower, and blowpit: packed tower, show that the value of chemical and heat recovery outweighs the total annual costs, thus giving rise to a net return or savings.

There is no appreciable chemical or heat recovery associated with the packed tower added to the acid tower, so net annual costs are the same as total annual costs.

FIGURE 12-1

MAINTENANCE COSTS OF
ELECTROSTATIC PRECIPITATORS

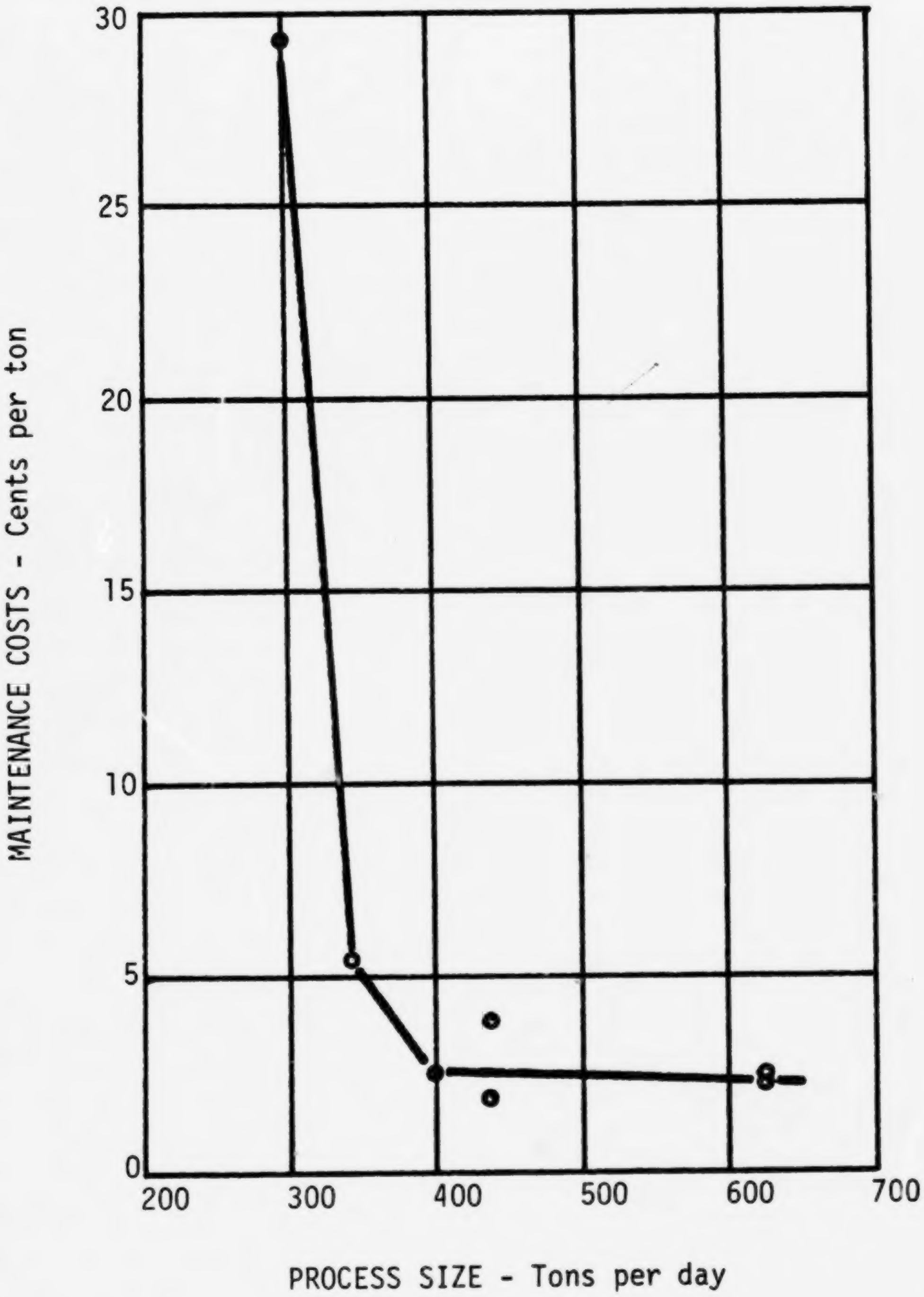

TABLE 12-5

AIR QUALITY CONTROL IN THE WOOD PULPING INDUSTRY ANNUAL MAINTENANCE COSTS FOR EQUIPMENT FOR KRAFT

Item	Annual Maintenance Cost
Noncondensible Gas Treatment:	
Lime Kiln Incineration	$ 15,600
Catalytic Oxidation	10,200
Scrubbers	1,920
Black Liquor Oxidation Units:	
Weak BLO	136,500
Concentrated BLO	136,500
Recovery Boilers:	
Electrostatic Precipitators (196 units)	1,607,200
Secondary Scrubbers on Elec. Ppts.	29,330
Secondary Scrubbers on Venturis	54,600
Dissolving Tank Vents:	
Mesh Pads	12,792
Packed Towers	2,625
Cyclonic Scrubbers	24,500
Lime Kiln Scrubbers:	
Venturi Scrubbers	9,680
Peabody & Similar Types	18,360
Cyclonic Scrubbers	11,000
Power Boiler Mechanical Collectors	832,800
	$2,903,607

TABLE 12-6

AIR QUALITY CONTROL IN THE WOOD PULPING INDUSTRY NET ANNUAL COST FOR EQUIPMENT FOR KRAFT

Item	Net Annual Cost
Noncondensible Gas Treatment	
Lime Kiln Incineration	$ 400,000
Catalytic Oxidation	100,000
Scrubbers	200,000
Black Liquor Oxidation Units	
Weak Black Liquor Oxidation	1,800,000
Concentrated Black Liquor Oxidation	2,500,000
Recovery Boilers	
Electrostatic Precipitators (196 units)	. . . . .*
Secondary Scrubber on Electrostatic Precipitators	400,000
Secondary Scrubbers on Venturis	500,000
Dissolving Tank Vents	
Mesh Pads	600,000
Packed Towers	35,000
Cyclonic Scrubbers	300,000
Lime Kiln Scrubbers	
Venturi Scrubbers	1,400,000
Peabody and Similar Types	2,600,000
Cyclonic Scrubbers	100,000
Power Boiler Mechanical Collectors	12,200,000
TOTAL	$23,135,000

*When credit is taken for the value of chemicals recovered by the precipitators, a net gain of about $7,600,000 is observed.

CHAPTER 13

FUTURE INDUSTRY INVESTMENT AND OPERATING COSTS

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CHAPTER 13

FUTURE INDUSTRY INVESTMENT AND OPERATING COSTS

SUMMARY

This chapter reports the rationale for and development of a model which provides data which can be used to project the investment and operating costs for emission control in the kraft pulping industry through 1980. Data are not available to perform similar analyses for sulfite and NSSC mills. A sensitivity analysis is also presented which suggests how the costs for emission control are influenced by emission standards, value of recoverable chemicals, and assumed rate of return.

To assist with the analysis, multi-path flow diagrams have been developed to indicate the various process alternatives which influence emissions. A simple program is presented to estimate total annual costs as a function of fixed and variable costs.

A mathematical programming model was developed and is presented by which it is possible, for any specified mill, to determine the optimal way to satisfy specified emission standards. The objective function is to maximize net revenue from emission control. Constraining functions include continuity from source to control, continuity from control to recovery, performance standards, control bounds, implicit integer constraints, and non-negativity restrictions. An example is analyzed with the model using the 1969 Oregon regulations. Costs for the example were based on prices of chemicals and equipment as of January 1969. As these prices change, the results of the analysis would also change.

13.1 INTRODUCTION

Investments and costs incurred by the industry for emission control are not uniform throughout the U. S. Emission limitations imposed by various authorities range from none to relatively strict. Few applicable regulations are in effect in the southeast where the great bulk of pulp production is concentrated. The trend, however, appears to be for more restrictive regulations.

This chapter reports the rationale for and development of a model which provides information which can be used to project the investment and operating costs needed for emission control in the kraft pulping industry through 1980. Sufficient data are not available to perform similar analyses for sulfite or NSSC mills. This chapter also presents a sensitivity analysis which determines how the costs for particulate emission control are influenced by emission standards and value of recoverable chemicals.

13.2 CONCEPTS FOR A MANAGEMENT MODEL

This chapter has as its objective to set forth a rational mechanism whereby the costs of emission control can be determined. Certain steps within the kraft system are there for the prime purpose of chemical recovery. Without chemical recovery (in the recovery furnace) the kraft process is not economically feasible. The critical issue is how far would the industry go in designing for chemical recovery in an unrestrained decision as opposed to how far it may be forced to go to satisfy emission constraints established by law. Such an analysis is presented in later sections.

To assist with this analysis a multi-path flow diagram for kraft processing was developed (Figure 13-1). This diagram represents a composite picture of kraft processes and indicates the various processing alternatives which influence emissions.

Figure 13-1 is to be interpreted as follows: solid line boxes represent distinct processing steps; "clouds" represent emissions. If there is no cloud attached to a solid line box it is concluded that no emissions are generated at that point. Numbers contained within the clouds refer to emission values contained in Table 13-1. If there are two numbers in the cloud this indicates that "yield" influences the emission. The upper number refers to the emission from a high yield mill, the lower number refers to that from a low yield mill. For purposes of this study low yield is defined to be less than 48 percent, high yield is said to be 48 percent or more.

An example will further illustrate interpretation of Figure 13-1. The first processing variable is batch versus continuous digestion. The number 1 (only one number) shown in the cloud attached to the turpentine condenser box indicates that emissions from that source are not influenced by yield nor are they influenced by the type of digester.

The eight lines in the center of the sheet show the many processing alternatives using weak and/or heavy BLO, et cetera. Looking at emissions from the D.C. evaporator-recovery furnace on the top two lines, one sees that there are two different numbers in each box. This means that yield influences the emissions from this processing step and also that the utilization of weak BLO will influence emissions

At the smelt dissolving tank there is only one number shown. This means that emissions from the smelt tank are independent of all other process alternates. The only other emission variable comes at the lime kiln where it is shown that incineration of noncondensible gases as well as yield affects emission values.

Power boilers, which are independent of processing alternates, are shown separately with emissions being dependent on type and quantity of fuel consumed. Some repetition is shown in the interest of simplifying flow paths.

Figure 13-2 indicates those sources emitting particulates and the control devices applicable for particulate control at each source. Figure 13-3 presents the same information for hydrogen sulfide and total organic sulfur compounds and Figure 13-4 is a similar presentation for sulfur dioxide.

TABLE 13-1

SOURCE ID	SOURCE NO.
XTURPENTINE CONDENSER-HIGH OR LOW YIELD	01
XHEAT ACCUMULATOR-HIGH OR LOW YIELD	02
XBATCH WASHERS-HIGH OR LOW YIELD	03
XCONTINUOUS WASHERS-HIGH OR LOW YIELD	04
XMULTIPLE EFFECT EVAPORATOR-HIGH OR LOW YIELD	05
XDC EVAPORATOR-RECOVERY BOILER-WITHOUT BLO-HIGH YIELD	06
XDC EVAPORATOR-RECOVERY BOILER-WITHOUT BLO-LOW YIELD	07
XWEAK BLACK LIQUOR OXIDATION-HIGH YIELD	08
XWEAK BLACK LIQUOR OXIDATION-LOW YIELD	09
XMULTIPLE EFFECT EVAPORATOR-HIGH OR LOW YIELD	10
XDC EVAPORATOR-RECOVERY BOILER WITH BLO-HIGH YIELD	11
XDC EVAPORATOR-RECOVERY BOILER WITH BLO-LOW YIELD	12
XCONCENTRATED BLO-HIGH YIELD	13
XCONCENTRATED BLO-LOW YIELD	14
XVENTURI EVAP/SCRUBBER WITHOUT BLO-HIGH YIELD	15
XVENTURI EVAP/SCRUBBER WITHOUT BLO-LOW YIELD	16
XVENTURI EVAP/SCRUBBER WITH BLO-HIGH YIELD	17
XVENTURI EVAP/SCRUBBER WITH BLO-LOW YIELD	18
XHIGH SOLIDS EVAPORATOR-HIGH OR LOW YIELD	19
XRECOVERY BOILER-HIGH OR LOW YIELD	20
XSMELT TANK-HIGH OR LOW YIELD	21
XSLAKE TANK-HIGH OR LOW YIELD	22
XLIME KILN WITHOUT INCINERATION-HIGH YIELD	23
XLIME KILN WITHOUT INCINERATION-LOW YIELD	24
XLIME KILN WITH INCINERATION-HIGH YIELD	25
XLIME KILN WITH INCINERATION-LOW YIELD	26
XPOWER BOILER-BARK	27
XPOWER BOILER-COAL	28
XPOWER BOILER-OIL	29
XPOWER BOILER-GAS	30

*EMICOEF	GASVOL	PARTICLE	HTWOS	TOTORGS	SOTWO
XSORC01	50.	0.	0.01	0.50	0.
XSORC02	300.	0.	0.1	3.20	0.01
XSORC03	97000.	0.	0.01	0.10	0.01
XSORC04	70000.	0.	0.02	0.22	0.02
XSORC05	50.	0.	0.40	0.50	0.01
XSORC06	280000.	93.	10.	1.00	3.3
XSORC07	420000.	140.	15.	1.50	5.0
XSORC08	9200.	0.0	0.02	0.40	0.0
XSORC09	13300.	0.0	0.02	0.40	0.0
XSORC10	30.	0.0	0.01	0.40	0.01
XSORC11	230000.	93.	1.0	0.70	3.3
XSORC12	420000.	140.	1.5	1.00	5.0
XSORC13	8400.	0.	0.01	0.30	0.0
XSORC14	12200.	0.	0.01	0.30	0.0
XSORC15	252000.	30.	10.	1.0	3.3
XSORC16	378000.	45.	15.	1.5	5.0
XSORC17	252000.	30.	1.0	0.70	3.3
XSORC18	378000.	45.	1.5	1.0	5.0
XSORC19	50.	0.	0.5	0.3	0.0
XSORC20	400000.	210.	0.1	0.0	4.4
XSORC21	45000.	? ~~4.0~~	0.04	0.06	0.0
XSORC22	7000.	4.0	0.0	0.0	0.0
XSORC23	31400.	39.0	0.8	0.46	3.0
XSORC24	40900.	51.0	1.0	0.6	4.0
XSORC25	31400.	39.0	0.8	0.54	3.0
XSORC26	40900.	51.0	1.0	0.70	4.0

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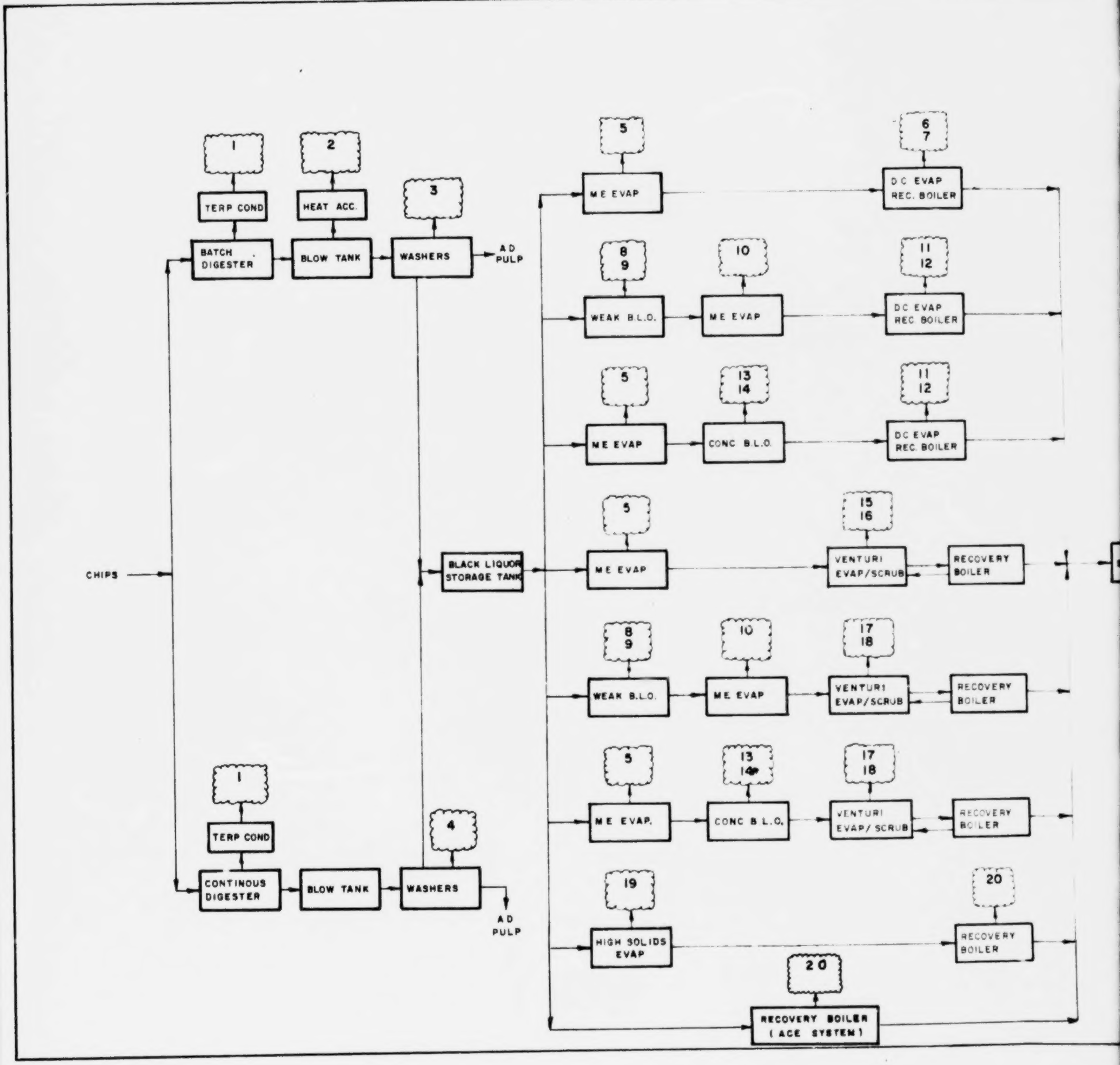
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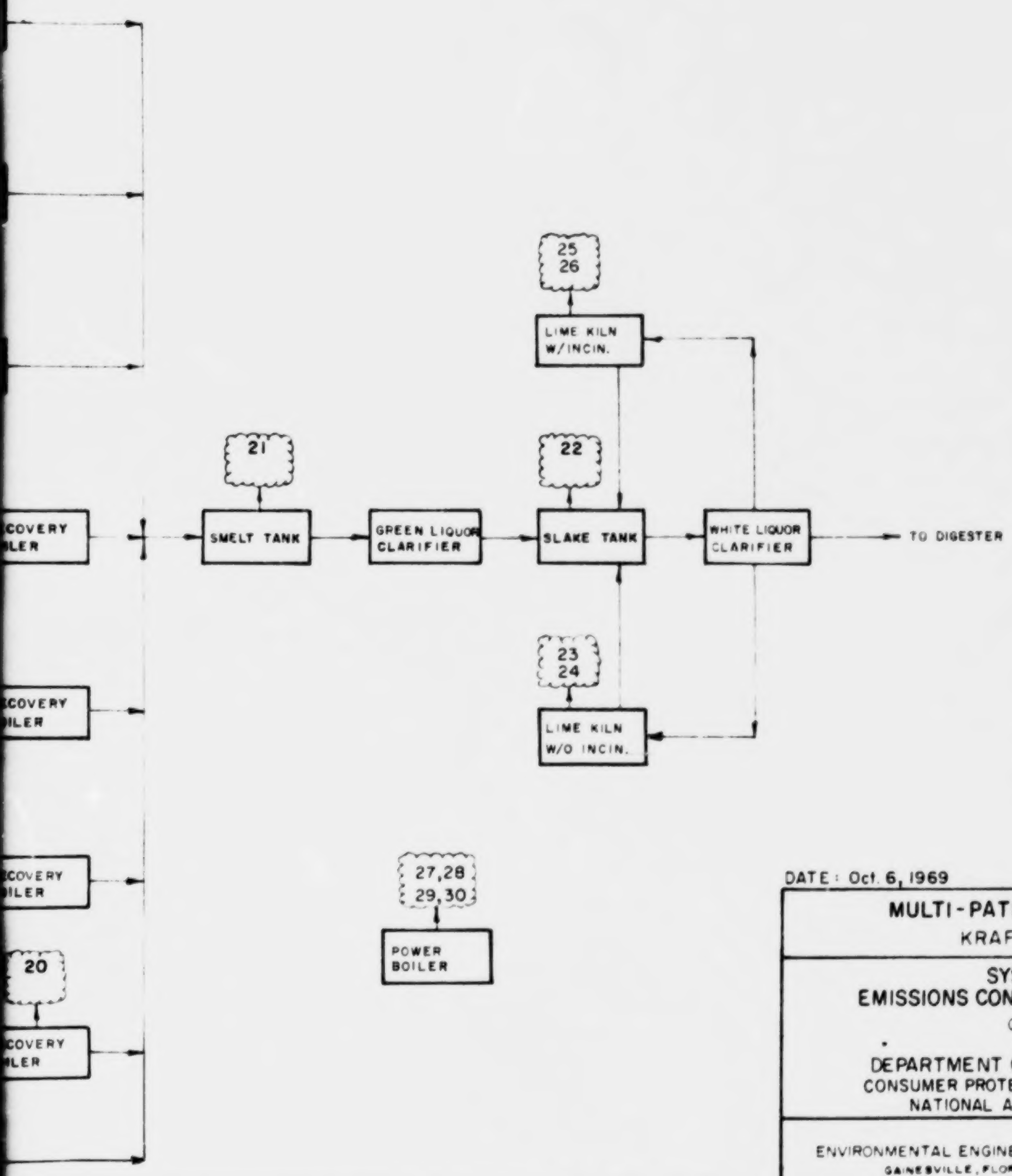
TERP COND
BATCH DIGESTER
2
HEAT ACC.
BLOW TANK
3
WASHERS
A D PULP
CHIPS
BLACK LIQUOR STORAGE TANK
1
TERP COND
CONTINOUS DIGESTER
BLOW TANK
4
WASHERS
A D PULP
5
M E EVAP
6 7
D C EVAP REC. BOILER
8 9
WEAK B.L.O.
10
M E EVAP
11 12
D C EVAP REC. BOILER
5
M E EVAP
13 14
CONC B.L.O.
11 12
D C EVAP REC. BOILER
5
M E EVAP
15 16
VENTURI EVAP/SCRUB
RECOVERY BOILER
8 9
WEAK B.L.O.
10
M E EVAP
17 18
VENTURI EVAP/SCRUB
RECOVERY BOILER
5
M E EVAP.
13 14
CONC B.L.O.
17 18
VENTURI EVAP/ SCRUB
RECOVERY BOILER
19
HIGH SOLIDS EVAP
20
RECOVERY BOILER
20
RECOVERY BOILER (ACE SYSTEM)

A


25
26
LIME KILN W/INCIN.
21
22
COVERY
BLER
SMELT TANK
GREEN LIQUOR CLARIFIER
SLAKE TANK
WHITE LIQUOR CLARIFIER
TO DIGESTER
23
24
COVERY
BILER
LIME KILN W/O INCIN.
COVERY
BILER
27,28
29,30
POWER BOILER
20
COVERY
ILER

DATE: Oct. 6, 1969

MULTI-PATH FLOW DIAGRAM
KRAFT PROCESSES

EXHIBIT NO
Fig. 13-1

SYSTEMS ANALYSIS STUDY OF
EMISSIONS CONTROL IN THE WOOD PULPING INDUSTRY
CONTRACT NO CPA 22-69-18
FOR
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
CONSUMER PROTECTION AND ENVIRONMENTAL HEALTH SERVICE
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION

ENVIRONMENTAL ENGINEERING, INC
GAINESVILLE, FLORIDA

J E SIRRINE COMPANY, ENGINEERS
GREENVILLE, S C

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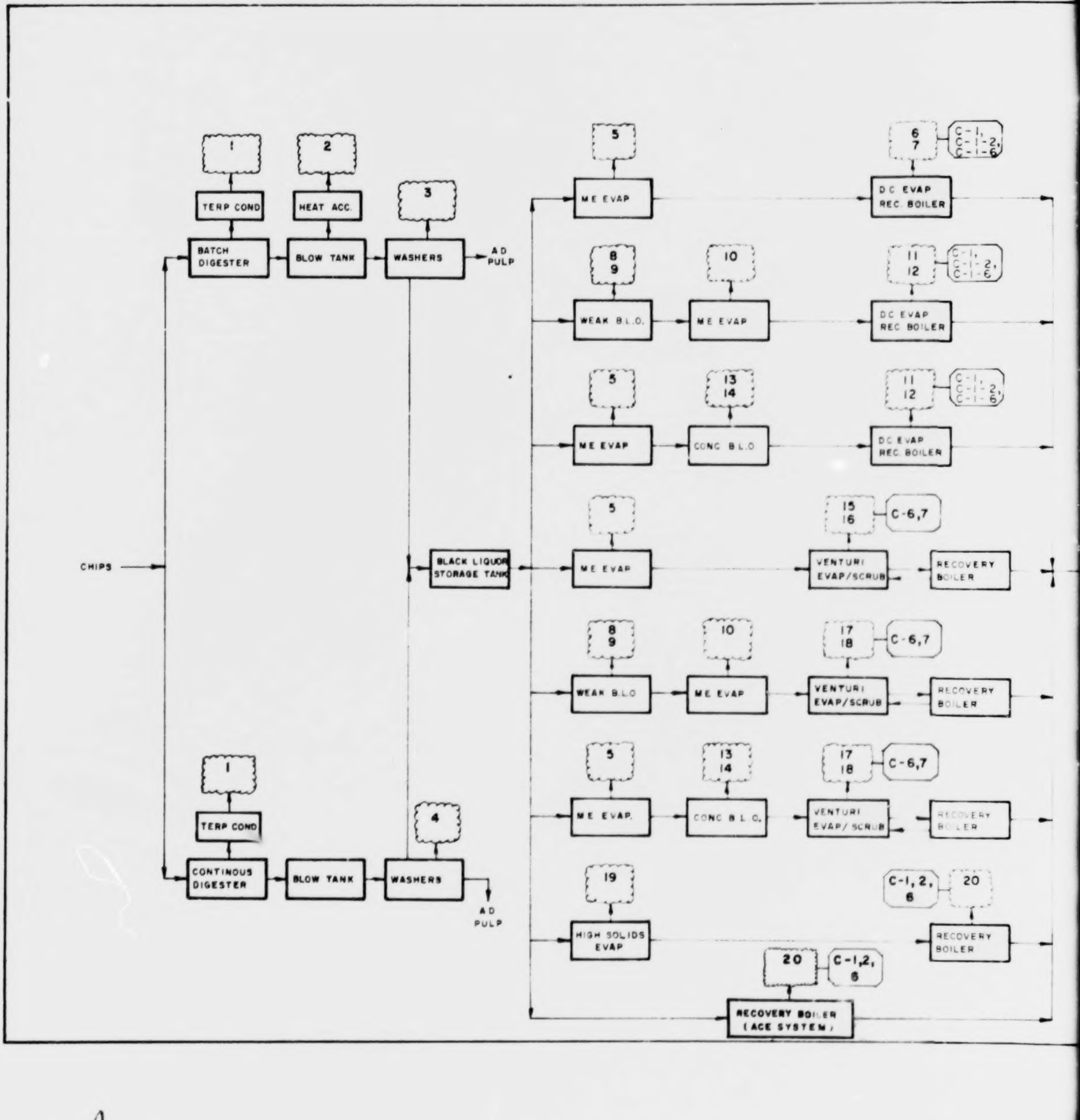

CHIPS
BATCH DIGESTER
TERP COND
1
BLOW TANK
HEAT ACC.
2
WASHERS
3
A D PULP
CONTINOUS DIGESTER
TERP COND
1
BLOW TANK
WASHERS
4
A D PULP
BLACK LIQUOR STORAGE TANK
M E EVAP
5
DC EVAP REC. BOILER
6 7
C-1, C-1-2, C-1-6
WEAK B.L.O.
8 9
M E EVAP
10
DC EVAP REC. BOILER
11 12
C-1, C-1-2, C-1-6
M E EVAP
5
CONC B.L.O.
13 14
DC EVAP REC. BOILER
11 12
C-1, C-1-2, C-1-6
M E EVAP
5
VENTURI EVAP/SCRUB
15 16
C-6,7
RECOVERY BOILER
WEAK B.L.O
8 9
M E EVAP
10
VENTURI EVAP/SCRUB
17 18
C-6,7
RECOVERY BOILER
M E EVAP.
5
CONC B L O.
13 14
VENTURI EVAP/ SCRUB
17 18
C-6,7
RECOVERY BOILER
HIGH SOLIDS EVAP
19
RECOVERY BOILER
20
C-1, 2, 6
RECOVERY BOILER (ACE SYSTEM)
20
C-1,2, 6

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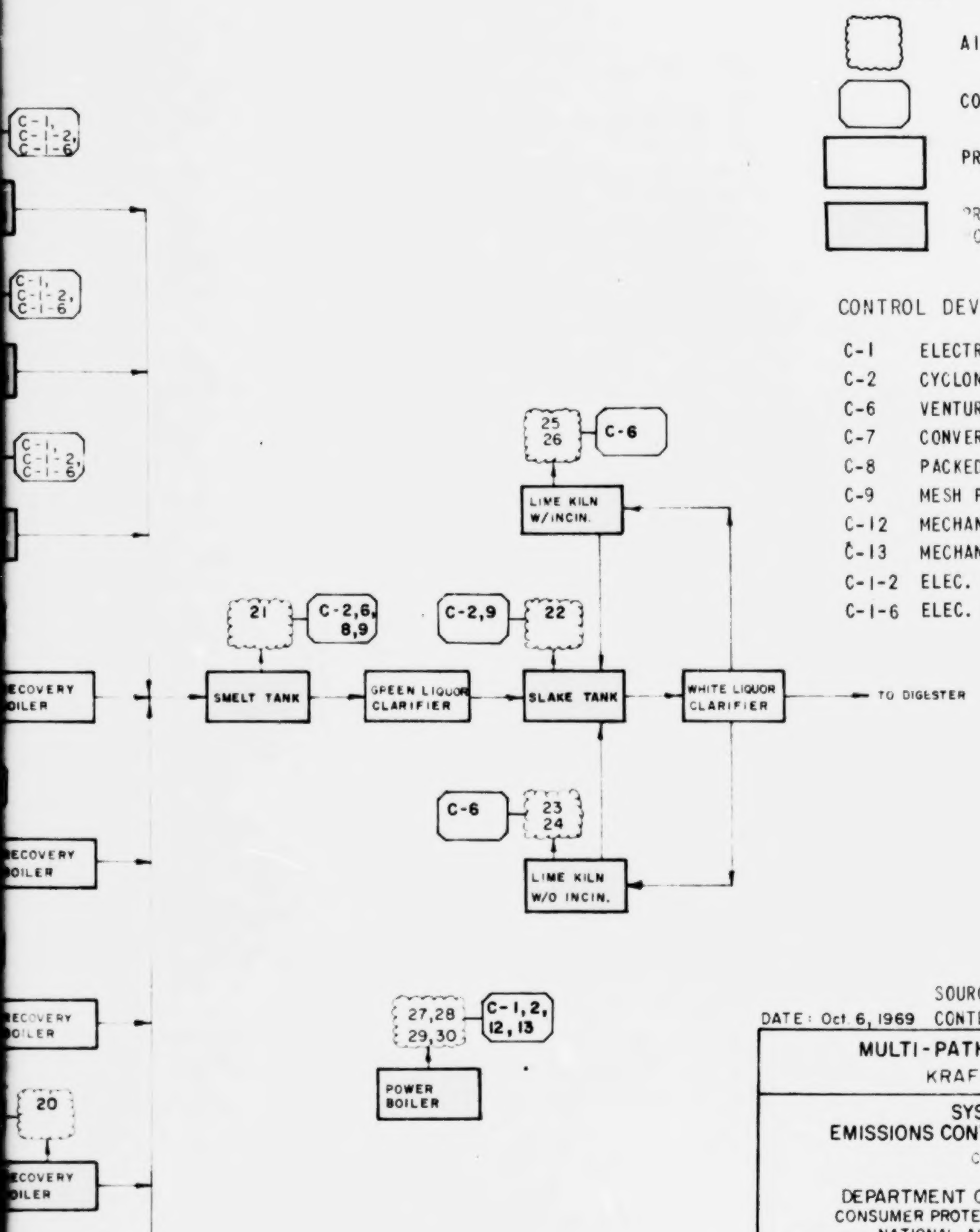
C-1,
C-1-2,
C-1-6
25
26
C-6
LIME KILN W/INCIN.
21
C-2,6, 8,9
C-2,9
22
ECOVERY OILER
SMELT TANK
GREEN LIQUOR CLARIFIER
SLAKE TANK
WHITE LIQUOR CLARIFIER
TO DIGESTER
C-6
23
24
LIME KILN W/O INCIN.
ECOVERY OILER
27,28
29,30
C-1,2, 12,13
POWER BOILER
20

SYMBOLS

AIR EMISSIONS

CONTROL DEVICE

PROCESS EQUIPMENT

PROCESS EQUIPMENT EMITTING PARTICULAR POLLUTANT

CONTROL DEVICES

C-1	ELECTROSTATIC PRECIPITATOR
C-2	CYCLONIC SCRUBBER
C-6	VENTURI SCRUBBER
C-7	CONVERT TO CYCLONIC EVAP. AND ADD PRECIPITATOR
C-8	PACKED TOWER SCRUBBER
C-9	MESH PAD
C-12	MECHANICAL COLLECTOR
C-13	MECHANICAL COLLECTOR PLUS SCRUBBER
C-1-2	ELEC. PPT. PLUS CYCLONIC SCRUBBER
C-1-6	ELEC. PPT. PLUS VENTURI SCRUBBER

SOURCES OF PARTICULATES AND APPLICABLE CONTROL DEVICES

DATE: Oct. 6, 1969

MULTI-PATH FLOW DIAGRAM
KRAFT PROCESSES

EXHIBIT NO
Fig. 13-2

SYSTEMS ANALYSIS STUDY OF
EMISSIONS CONTROL IN THE WOOD PULPING INDUSTRY
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FOR
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CONSUMER PROTECTION AND ENVIRONMENTAL HEALTH SERVICE
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ENVIRONMENTAL ENGINEERING, INC
GAINESVILLE, FLORIDA

J. E. SIRRINE COMPANY, ENGINEERS
GREENVILLE, S.C.

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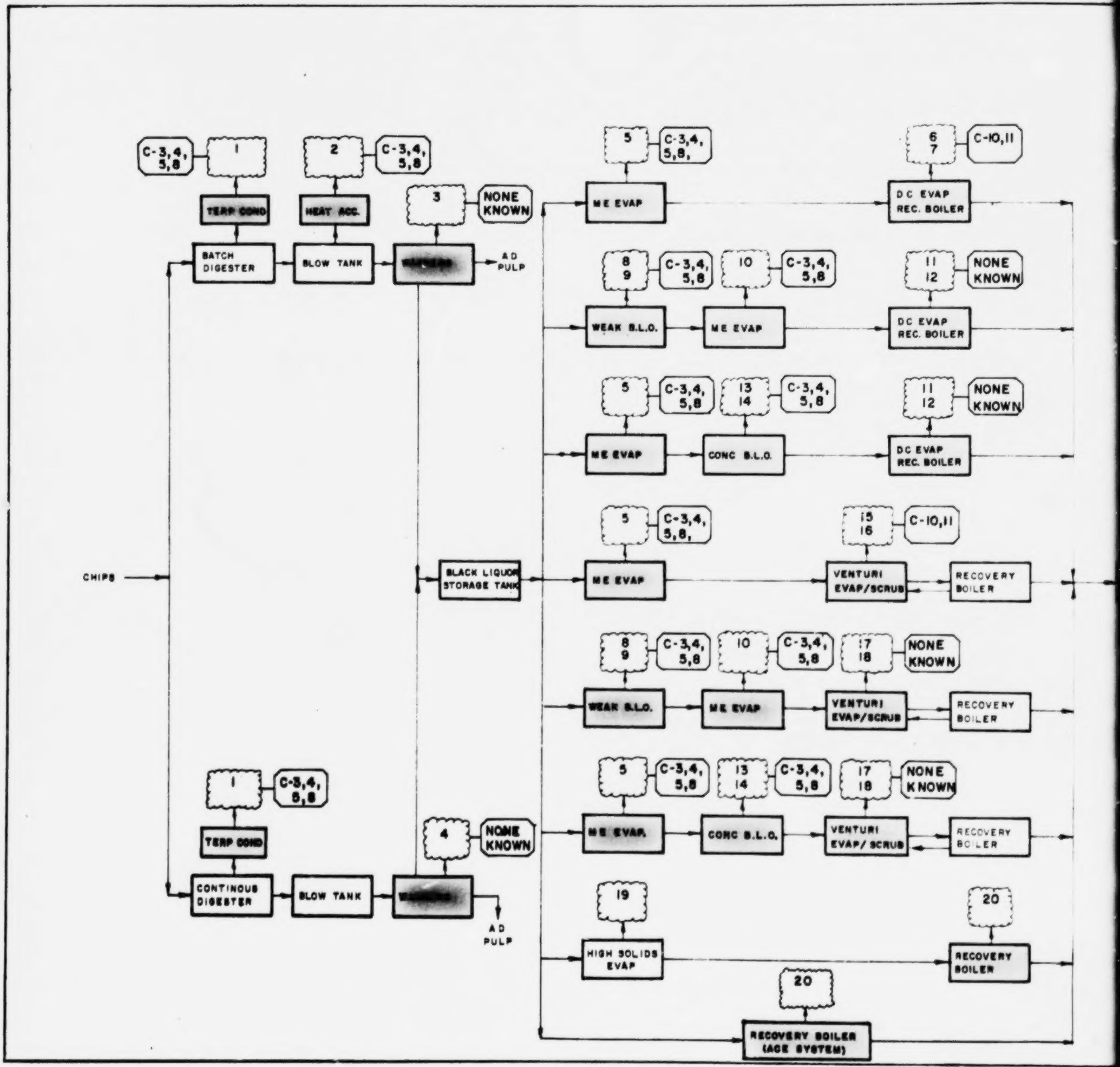
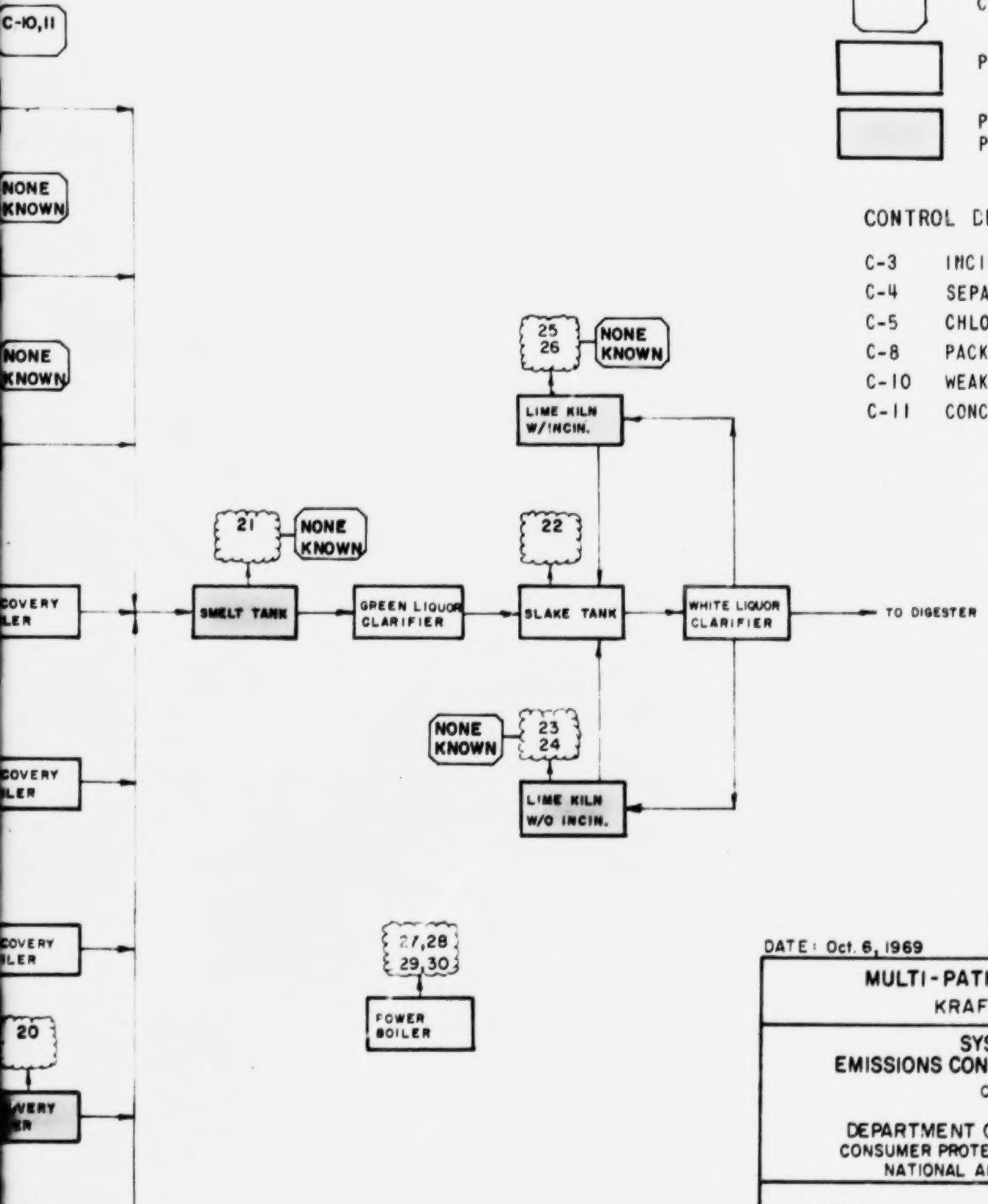

C-3,4, 5,8
1
TERP COND
BATCH DIGESTER
2
HEAT ACC.
C-3,4, 5,8
BLOW TANK
3
NONE KNOWN
WASHERS
AD PULP
5
C-3,4, 5,8,
ME EVAP
6 7
C-10,11
DC EVAP REC. BOILER
8 9
C-3,4, 5,8
10
C-3,4, 5,8
11 12
NONE KNOWN
WEAK B.L.O.
ME EVAP
DC EVAP REC. BOILER
5
C-3,4, 5,8
13 14
C-3,4, 5,8
11 12
NONE KNOWN
ME EVAP
CONC B.L.O.
DC EVAP REC. BOILER
CHIPS
BLACK LIQUOR STORAGE TANK
5
C-3,4, 5,8,
ME EVAP
15 16
C-10,11
VENTURI EVAP/SCRUB
RECOVERY BOILER
8 9
C-3,4, 5,8
10
C-3,4, 5,8
17 18
NONE KNOWN
WEAK B.L.O.
ME EVAP
VENTURI EVAP/SCRUB
RECOVERY BOILER
1
C-3,4, 5,8
TERP COND
5
C-3,4, 5,8
13 14
C-3,4, 5,8
17 18
NONE KNOWN
4
NONE KNOWN
ME EVAP.
CONC B.L.O.
VENTURI EVAP/ SCRUB
RECOVERY BOILER
CONTINOUS DIGESTER
BLOW TANK
WASHERS
AD PULP
19
HIGH SOLIDS EVAP
20
RECOVERY BOILER
20
RECOVERY BOILER (ACE SYSTEM)

A


C-10,11
NONE KNOWN
NONE KNOWN
25
26
NONE KNOWN
LIME KILN W/INCIN.
21
NONE KNOWN
22
COVERY
LER
SMELT TANK
GREEN LIQUOR CLARIFIER
SLAKE TANK
WHITE LIQUOR CLARIFIER
TO DIGESTER
NONE KNOWN
23
24
LIME KILN W/O INCIN.
COVERY
LER
COVERY
LER
27,28
29,30
POWER BOILER
20
VERY
ER

SYMBOLS

☁ AIR EMISSIONS

⬡ CONTROL DEVICE

▢ PROCESS EQUIPMENT

▨ PROCESS EQUIPMENT EMITTING PARTICULAR POLLUTANT

CONTROL DEVICES

C-3	INCINERATION IN LIME KILN
C-4	SEPARATE INCINERATION
C-5	CHLORINATION
C-8	PACKED TOWER SCRUBBER
C-10	WEAK B.L.O.
C-11	CONCENTRATED B.L.O.

NOTE: WHEN INCINERATION IN LIME KILN IS USED IT IS ASSUMED THAT SOURCES 1, 2, 5, 8, 9, 10, 13, & 14 ARE ALL TREATED TOGETHER.

DATE: Oct. 6, 1969

SOURCES OF H_2S AND ORGANIC SULFUR COMPOUNDS AND APPLICABLE CONTROL DEVICES

MULTI-PATH FLOW DIAGRAM
KRAFT PROCESSES

EXHIBIT NO
Fig. 13-3

SYSTEMS ANALYSIS STUDY OF
EMISSIONS CONTROL IN THE WOOD PULPING INDUSTRY
CONTRACT NO CPA 22-69-18
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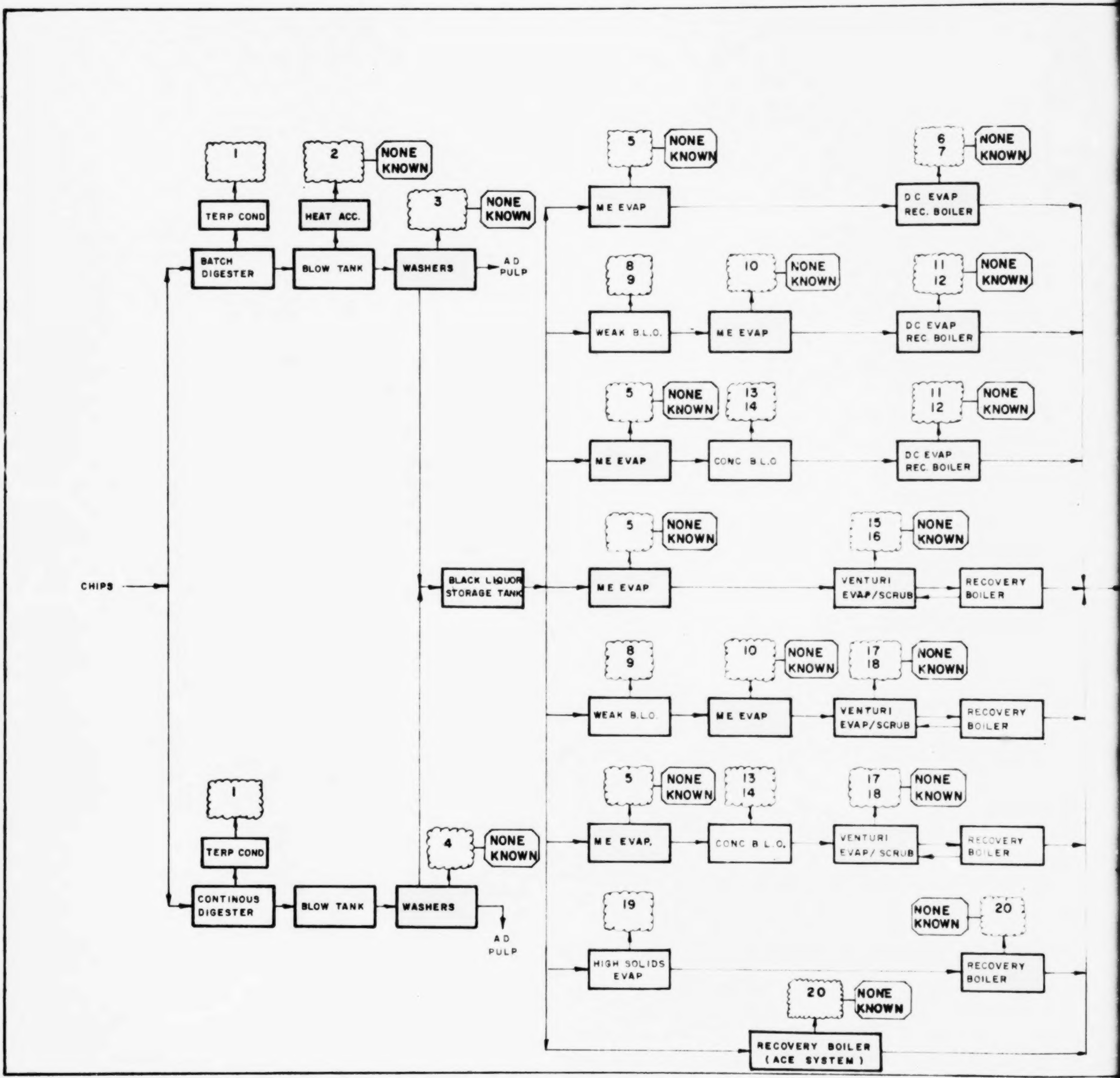
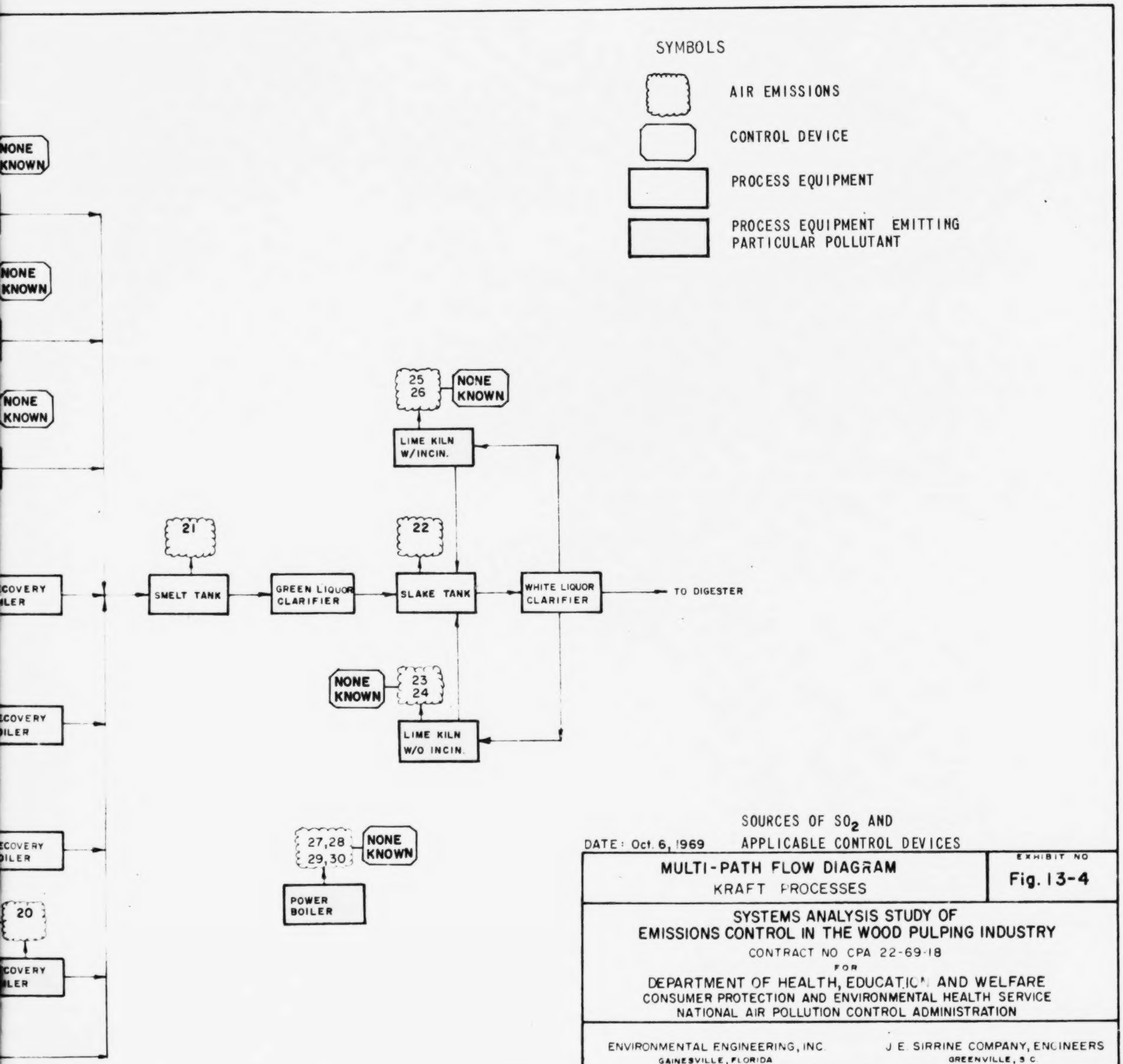
J. E. SIRRINE COMPANY, ENGINEERS
GREENVILLE, S.C.

B


CHIPS
BATCH DIGESTER
TERP COND
1
BLOW TANK
HEAT ACC.
2
NONE KNOWN
WASHERS
3
NONE KNOWN
A D PULP
CONTINOUS DIGESTER
TERP COND
1
BLOW TANK
WASHERS
4
NONE KNOWN
A D PULP
BLACK LIQUOR STORAGE TANK
M E EVAP
5
NONE KNOWN
DC EVAP REC. BOILER
6 7
NONE KNOWN
WEAK B.L.O.
8 9
M E EVAP
10
NONE KNOWN
DC EVAP REC. BOILER
11 12
NONE KNOWN
M E EVAP
5
NONE KNOWN
CONC B.L.O.
13 14
DC EVAP REC. BOILER
11 12
NONE KNOWN
M E EVAP
5
NONE KNOWN
VENTURI EVAP/SCRUB
15 16
NONE KNOWN
RECOVERY BOILER
WEAK B.L.O.
8 9
M E EVAP
10
NONE KNOWN
VENTURI EVAP/SCRUB
17 18
NONE KNOWN
RECOVERY BOILER
M E EVAP.
5
NONE KNOWN
CONC B.L.O.
13 14
VENTURI EVAP/ SCRUB
17 18
NONE KNOWN
RECOVERY BOILER
HIGH SOLIDS EVAP
19
NONE KNOWN
20
RECOVERY BOILER
20
NONE KNOWN
RECOVERY BOILER (ACE SYSTEM)

A


SYMBOLS
AIR EMISSIONS
CONTROL DEVICE
PROCESS EQUIPMENT
PROCESS EQUIPMENT EMITTING PARTICULAR POLLUTANT
NONE KNOWN
NONE KNOWN
NONE KNOWN
25 26
NONE KNOWN
LIME KILN W/INCIN.
21
22
ECOVERY ILER
SMELT TANK
GREEN LIQUOR CLARIFIER
SLAKE TANK
WHITE LIQUOR CLARIFIER
TO DIGESTER
NONE KNOWN
23 24
LIME KILN W/O INCIN.
ECOVERY DILER
ECOVERY DILER
27,28 29,30
NONE KNOWN
POWER BOILER
20
ECOVERY ILER

SOURCES OF SO_2 AND APPLICABLE CONTROL DEVICES

DATE: Oct. 6, 1969

MULTI-PATH FLOW DIAGRAM
KRAFT PROCESSES

EXHIBIT NO
Fig. 13-4

SYSTEMS ANALYSIS STUDY OF
EMISSIONS CONTROL IN THE WOOD PULPING INDUSTRY
CONTRACT NO CPA 22-69-18
FOR
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
CONSUMER PROTECTION AND ENVIRONMENTAL HEALTH SERVICE
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION

ENVIRONMENTAL ENGINEERING, INC.
GAINESVILLE, FLORIDA

J. E. SIRRINE COMPANY, ENGINEERS
GREENVILLE, S.C.

B

13.3 ANALYSIS OF EMISSION SOURCES AND CONTROLS

In the preceding chapters of this report extensive cost data for the alternative control schemes available to the wood pulping industry have been brought together. It was found that the technology for control of particle emissions is well established and that the use of "add-on" devices can be effective for this type of control.

Chlorination, packed tower scrubbing and lime kiln incineration were shown to be practical methods for the control of H_2S and other organic sulfur compounds being emitted from digesters, blow tanks, and multiple effect evaporators. The effectiveness of lime kiln incineration could be expected to approach 100 percent; chlorination and packed tower scrubbing are considered less effective. Therefore, with standards specifying that malodorous compounds must be controlled by a method equally as effective as lime kiln incineration, it becomes apparent that only incineration can be considered as a feasible solution.

For pulp washers, smelt tanks, and lime kilns there are no known add-on devices, which can be utilized for the control of malodorous emissions. It seems reasonable to think that scrubbers at smelt tanks and lime kilns would have some effect on the emission of H_2S and other sulfur compounds but to date, data are lacking which would give a clue to the effectiveness of these devices on odors. Apparently, the only practical way to control emissions of H_2S and organic sulfur compounds is to assure nearly 100 percent oxidation within the kiln itself.

Chapter 6 makes reference to some new process technology which might be applicable to pulp washers. The conclusion drawn is that diffusion washing and pressure washing appear to have significant future potential.

The installation of weak or heavy black liquor oxidation can be considered as a control option for application to D.C. evaporator-recovery furnace installations and Venturi evaporator/scrubbers. If emissions still exceed limits imposed by the regulations and a fairly new furnace is in operation, an option might be conversion to one of the new high solids evaporator designs and modification of the DC evaporator. If an older furnace is in use, the only alternative may be installation of a new recovery system in which contact between flue gas and black liquor is eliminated.

No feasible methods for control of SO_2 were identified. A detailed discussion of sulfur recovery and control schemes for power boilers was presented in Chapter 8. From this discussion, it is concluded that if there are no feasible schemes for the control of SO_2 at power plant scale then surely it is difficult to expect feasible control to be effected on the more dilute process streams.

Control methods applicable to power boilers are effective only in the removal of particulates. None of the methods investigated would be effective in reducing emission of sulfur compounds. The conclusion drawn in Chapter 5 is that due to the range of operating efficiencies and costs, the selection of the most effective control method would have to be determined for each individual case.

13.3.1 COSTS OF CONTROL METHODS

The total cost of a given control can be partitioned into a fixed cost and a variable cost. It is being assumed that the fixed costs are comprised of the amortized capital investment, taxes, insurance, and administrative cost. Variable costs consist of direct operational costs as itemized in Chapter 5 and include labor (including overhead), raw materials and chemicals, utilities, maintenance and supplies, and waste disposal.

A simple program has been written using the MARVEL language associated with the IBM MPS/360 system to determine the total annual costs as a function of the selected rate of return, service life, administrative costs, and taxes and insurance.

Let

U_{1j} = Total annual cost of control j

U_{2j} = Direct operating cost of control j

U_{3j} = Direct capital cost of control j

n_j = Service life of control j

i_j = Rate of return for control j

A_{1j} = Ratio of indirect capital costs to U_{3j} for control j

A_{2j} = Ratio of taxes and insurance to U_{3j} $(1+A_{1j})$ for control j

A_{3j} = Ratio of administrative cost to U_{3j} $(1+A_{1j})$ for control j

Then, the total annual cost of control j, U_{1j}, can be expressed as

$$U_{1j} = U_{2j} + (1+A_{1j})\, U_{3j} \left\{ A_{2j} + A_{3j} + [i_j(1+i_j)^{n_j}] \Big/ [(1+i_j)^{n_j} -1] \right\}$$

Eq. 13.1

For the calculations to date, indirect costs have been assumed to equal 20 percent of direct capital costs (A_{1j} = 0.20 for all j); taxes and insurance are 2 percent of total capital costs (A_{2j} = 0.02 for all j); and administrative costs are assumed to equal 5 percent of total capital cost (A_{3j} = 0.05 for all j). Also rates of return of 10 percent (i_j = 0.10 for all j) and 20 percent (i_j = 0.20 for all j) have been used. The direct operating cost, U_{2j}, can be expressed as a function of gas flow in CFM. Likewise, the cost functions for direct capital costs can be presented as a function of gas flow in CFM. A sample printout from the program is presented as Table 13-2.

All costs are based on the price of chemicals and equipment as of January 1969. As these prices change, the results of the analysis would also change.

Using equation 13.1 and knowing the relationships for direct operating costs and direct capital costs, it is possible to estimate the total annual costs directly for a relatively wide variety of assumed conditions. These cost data also are used to determine the fixed and variable costs for the optimization model. However, the measure of effectiveness in the optimization model is ability to remove the particular commodity of interest. Also, it is desired to depict the unit's actual capability as accurately as possible so it is preferred to use the annual operating efficiency rather than total efficiency.

TABLE 13-2

COST ANALYSIS OF CONTROL METHODS

```
THIS REPORT CONTAINS A COST ANALYSIS OF THE FOLLOWING CONTROL

CONTROL                          CONTROL IDENTIFICATION                              TOTAL
NUMBER                                                                                EFF.

 1-1       'X99.0% GUARANTEED PRECIP. ADD TO EXIST. 90% PRECIP. ON GRND.'            99.0


THE FOLLOWING RESULTS ARE PRESENTED


1.ITEMIZED CAPITAL COSTS


2.ITEMIZED DIRECT OPERATING COSTS


3.ITEMIZED TOTAL ANNUAL COSTS FOR RATE OF RETURN BEFORE TAXES = 10%


4.TOTAL ANNUAL COST FOR RATES OF RETURN FROM 0% TO 20%
```

```
EXECUTOR.     MPS/360 V2-M6
```

TABLE 13-2 (continued)

```
                ASSUMPTIONS

     A.INDIRECT COSTS = 20% OF DIRECT CAPITAL COSTS

     B.TAXES AND INSURANCE = 2% OF TOTAL CAPITAL COST

     C.ADMINISTRATIVE COSTS = 5% OF TOTAL CAPITAL COST

     D.SERVICE LIFE =    10 YEARS

            1.ITEMIZED CAPITAL COSTS

                                         CAPITAL COST($)
        COST ITEM
                                  *100000CFM***200000CFM***300000CFM***400000CFM**
'1.PURCHASED EQUIPMENT'            135200.0    212840.0    297050.0    370670.0
'2.EQUIPMENT ERECTION'              79680.0    150700.0    207900.0    261050.0
'3.EQUIP.FOUNDATION & BLD.'         68000.0     81000.0     88000.0    108000.0
'4.PROCESS & INST. PIPING'          39000.0     67000.0     93000.0    117000.0
'5.POWER WIRING & LIGHTING'         12000.0     12500.0     13300.0     15000.0
'6.TOTAL DIRECT CAPITAL COST'      333880.0    524040.0    699250.0    871720.0
'7.TOTAL CAPITAL COST'             400655.9    628847.9    839099.8   1046063.8


            2.ITEMIZED DIRECT OPERATING COST

                                   DIRECT OPERATING COST($/YR)
        COST ITEM
                                  *100000CFM***200000CFM***300000CFM***400000CFM**
'1.LABOR,INCLUDING OVERHEAD'         2000.0      2000.0      2000.0      2000.0
'2.RAW MATERIALS & CHEMICALS'
'3.WATER'
'4.ELECTRICITY'                      2650.0      5260.0      7770.0     10310.0
'5.STEAM'
'6.MISCELLANEOUS UTILITIES'
'7.MAINTENANCE & SUPPLIES'           6760.0      9630.0     13010.0     17450.0
'8.WASTE DISPOSAL'
'9.OTHER'
'10.TOT.DIRECT OPERATING COST'      11410.0     16890.0     22780.0     29760.0
```

TABLE 13-2 (continued)

```
                   3.ITEMIZED TOTAL ANNUAL COST FOR RATE OF
                     RETURN = 10%

                                        TOTAL ANNUAL COST($1YR)
         COST ITEM
                               *100000CFM***200000CFM***300000CFM***400000CFM**
'1.DIRECT OPERATING COST'         11410.0      16890.0      22780.0      29760.0
'2.TAXES & INSURANCE'              8013.1      12577.0      16782.0      20921.3
'3.ADMINISTRATIVE COSTS'          20032.8      31442.4      41955.0      52303.2
'4.DEPRECIATION'                  65306.9     102502.2     136773.3     170508.4
'5.TOTAL ANNUAL COST'            104762.8     163411.5     218290.2     273492.8


                   4.TOTAL ANNUAL COST FOR RATES OF RETURN
                     FROM 0% TO 20%

                   FUNCTIONAL RELATIONSHIP

     TOTAL ANNUAL COST = DIRECT OPERATING COST + TAXES & INSURANCE +
                         ADMINISTRATIVE COST  + CAPITAL COST*(XI(1.+X
                         ((1.+XI)**XN-1.)

                   WHERE XI= RATE OF RETURN
                         XN= SERVICE LIFE IN YEARS

               **100000CFM*****200000CFM*****300000CFM*****400000CFM*
     RATE OF   TOTAL ANNUAL  TOTAL ANNUAL  TOTAL ANNUAL  TOTAL ANNUAL
     RETURN     COST($1YR)    COST($1YR)    COST($1YR)    COST($1YR)
                  39455.9       60909.3       81516.9      102984.4
       .02        84055.5      130918.3      174933.1      219441.7
       .04        88835.1      138440.6      184970.4      231954.7
       .06        93392.5      146350.1      195524.3      245111.8
       .08        99155.4      154626.2      206567.6      258878.8
       .10       104655.9      163251.7      218076.9      273227.0
       .12       110355.6      172205.4      230024.3      288121.1
       .14       116207.1      181468.2      242384.0      303529.4
       .16       122352.0      191018.6      255127.6      319416.2
       .18       128507.8      200837.3      268229.1      335749.1
       .20       135021.4      210903.8      281661.3      352494.4
```

It is assumed that the desired percent removal at a given source will be in the range of the available control equipment and that any percent removal can be utilized within that range; e.g., a 97.8 percent precipitator. Consequently, it is possible to aggregate those control methods which differ only in the percent removal into an equivalent single control with a fixed cost and a variable cost as a function of the quantity removed.

13.3.2 OPTIMIZATION MODEL

The objective of the mathematical programming model is to determine, for any specified pulp mill, the optimal way to satisfy the specified standards. This constrained optimization technique is comprised of an objective function and a set of constraints. The interested reader is referred to texts on mathematical programming for a more detailed description (1, 2).

A literature review was made to determine whether suitable mathematical models had been developed by others. Teller (3) reports the use of linear programming to examine the costs of alternative air pollution abatement policies in an urban area. Norsworthy (4), and Burton and Sanjour (5) have also presented the results of their analyses of urban air pollution problems. Correspondence with NCASI and NAPCA personnel did not uncover any specific references to emissions control modeling in the pulping industry. D. H. Moreau (6) has devised a nonlinear programming model for water pollution control in an unbleached kraft mill. Based on the unavailability of directly relevant models it appeared that it would be best to devise a new model for analyzing emission control in the pulp industry.

It was felt that the model should be able to analyze simultaneously multiple emission sources of one or more commodities. Performance standards can be formulated either on a source-by-source basis (equiproportional abatement) or by specifying an allowable level of emissions from all sources (selective abatement). Also, provision needs to be made for analyzing the trade-offs that exist between the removal of a specified pollutant(s) and the generation and/or removal of other pollutants.

The components of the mathematical programming model are described below in algebraic form. The notation is presented in Table 13-3. Following presentation of the entire model, procedures for decomposing the model will be discussed.

TABLE 13-3

NOTATION FOR OPTIMIZATION MODEL

Symbol	Definition
$y_{ij}^{(k)}$	interger variable associated with entering the k^{th} commodity into the j^{th} control at the i^{th} source. $y_{ij}^{(k)} = o,1$.
$x_{ijl}^{(k)}$	quantity of commodity k entering the l^{th} removal range in the j^{th} control at the i^{th} source.
$c_{ijl}^{(k)}$	unit cost of routing commodity k into l^{th} removal range in the j^{th} control at the i^{th} source.
$z_{ijo}^{(k)}$	quantity of commodity k going from the j^{th} control at the i^{th} source to the atmosphere, o.
$z_{ij}^{(k)}$	quantity of commodity k leaving j^{th} control at the i^{th} source.
$a_{i}^{(k)}$	quantity of commodity k produced at the i^{th} source per unit of pulp tonnage.
$\bar{a}_{i}^{(k)}$	allowable quantity of commodity k which can be emitted at the i^{th} source per unit of pulp tonnage.
$\rho_{ijl}^{(k'k)}$	quantity of another commodity, k, produced or removed per unit of $x_{ijl}^{(k')}$.
$p_{ij}^{(k)}$	price per ton of commodity k recovered from the j^{th} control at the i^{th} source.
$f_{ij}^{(k)}$	fixed cost for routing commodity k to control j at source i.
$\bar{\gamma}_{ijl}^{(k)}$	upper bound on percent removal of commodity k in the l^{th} removal range of the j^{th} control at the i^{th} source.

13.3.2.1 Continuity From Source to Control

$$\sum_{j=1}^{q} y_{ij} = 1.0 \text{ for } i = 1,\cdots,p$$

Eq. 13.2

Equation 13.2 denotes that a control is used at each of the i sources.

Equation 13.3 denotes that the emissions from a mill producing B tons of pulp per day, $a_i^{(k)}$ B, go to either one of the controls, $x_{ijl}^{(k)}$, or are emitted to the atmosphere, $z_{ijo}^{(k)}$. It is possible that a given control for commodity k may introduce, or remove another commodity k', so that the $\rho_{ijl}^{(k'k)} x_{ijl}^{(k')}$ term is included.

$$\rho_{ijl}^{(k'k)} x_{ijl}^{(k')} + \sum_{l=1}^{t} x_{ijl}^{(k)} + z_{ijo}^{(k)} = a_i^{(k)} B$$

$$\text{for } i = 1,\cdots,p \quad k = 1,\ldots,u$$

Eq. 13.3

13.3.2.2 Continuity From Control to Recovery

It is convenient to determine the total amount of recovered chemicals, $z_{ij}^{(k)}$, which is the sum of commodity flows to the various controls, or

$$-\sum_{l=1}^{t} x_{ijl}^{(k)} + z_{ij}^{(k)} = 0$$

$$\text{for } i = 1,\cdots,p;\ j = 1,\cdots,q;\ k = 1,\cdots,u$$

Eq. 13.4

13.3.2.3 Performance Standards

a. Equiproportional Abatement

$$\sum_{j=1}^{q} z_{ijo}^{(k)} \leqq \bar{a}_i^{(k)} B$$

for $i = 1,\cdots,p$; $k = 1,\cdots,u$

Eq. 13.5

b. Selective Abatement

$$\sum_{i=1}^{p} \sum_{j=1}^{q} z_{ijo}^{(k)} \leqq B \sum_{i=1}^{p} \bar{a}_i^{(k)}$$

for $k = 1,\cdots,u$

Eq. 13.6

13.3.2.4 Control Bounds

A given removal range can control only a specified amount of a given commodity $a_i^{(k)} (\bar{\gamma}_{ijl}^{(k)}) B$, at a given unit cost. This bound is expressed in constraint 13.7.

$$- [a_i^{(k)} (\bar{\gamma}_{ijl}^{(k)}) B] y_{ij}^{(k)} + x_{ijl}^{(k)} \leqq 0$$

for $i = 1,\cdots,p$; $j = 1,\cdots,q$;
$l = 1,\cdots,t$; $k = 1,\cdots,u$

Eq. 13.7

13.3.2.5 Implicit Integer Constraints

If the fixed charge is included, then we require that $y_{ij}^{(k)} = 0$ or 1. Thus, if a given control is selected, then the full fixed charge is assessed. In a linear programming format, this restriction can be written as

$$0 \leqq y_{ij}^{(k)} \leqq 1.0$$

$$\text{for } i = 1,\cdots\cdots,p;\ j = 1,\cdots\cdots,q;\ k = 1,\cdots\cdots,u$$

Eq. 13.8

and the usual optimization procedure is modified so that $y_{ij}^{(k)}$ is either 0 or 1.

13.3.2.6 Nonnegativity Restrictions

Lastly, we require that all of the variables be nonnegative.

$$x_{ijl}^{(k)},\ z_{ijo}^{(k)},\ z_{ij}^{(k)} \geqq 0$$

$$\text{for all } i,\ j,\ k,\ l$$

Eq. 13.9

13.3.2.7 Decomposing The Problem

The problem is set up so that it can handle many of the complexities arising in actual cases. However, it is sometimes possible to divide the single large problem into smaller independent sub-problems under specified conditions. These possible simplifications are outlined below.

13.3.2.7.1 No Commodity Interdependencies

If each commodity is emitted and/or controlled independent of the presence of the other commodities, then an optimal control strategy can be determined for each commodity independently. Mathematically, this means that $\rho_{ijl}^{(k'k)} = 0$ for all k in Eq. 13.3.

13.3.2.7.2 Equiproportional Abatement Formulation

If equiproportional abatement type of performance standards are employed, then an optimal control program can be specified for each source independent of the other sources.

13.3.2.8 Objective Function

The objective is to maximize the net revenue from emission control. Negative revenues indicate a positive control cost. The objective function is

$$\text{Max.}Z = \sum_{i=1}^{p} \sum_{j=1}^{q} \sum_{k=1}^{u} p_{ij}^{(k)} z_{ij}^{(k)} - \sum_{i=1}^{p} \sum_{j=1}^{q} \sum_{k=1}^{u} f_{ij}^{(k)} y_{ij}^{(k)} - \sum_{i=1}^{p} \sum_{j=1}^{q} \sum_{l=1}^{t} \sum_{k=1}^{u} c_{ijl}^{(k)} x_{ijl}^{(k)}$$

Eq. 13.10

The first term on the right hand side represents the gross revenue from recovered chemicals. The middle term is the fixed cost and last term is the variable costs.

13.3.3 ANALYSIS OF COST IMPACT

There is some level of particulate control which is sought voluntarily by the industry because the value of recovered chemical offsets the cost of collection. This is not the case, however, when consideration is given to control of emissions of H_2S, organic sulfur compounds, or SO_2. There are no directly measurable savings which accrue as a result of controlling these emissions. It must be concluded, therefore, that virtually all costs incurred in reducing other than particulate emissions should be looked upon as direct costs of pollution control.

The cost impact analysis is made of a mill of specified size, technology, and yield. Availability of control devices depends on the technology under consideration. The analysis of cost impact includes consideration of the value of recovered chemicals and existing control equipment. Performance standards must be specified for each indicated constituent either at each source or as an allowable emission from all sources.

It was decided to analyze high and low yield mills producing 300 tons/day, 500 tons/day, and 1000 tons/day of pulp. It is assumed that the pulp industry will select the most effective strategy for emission control. If there are no recovered chemicals, then the problem can be reduced to minimizing the cost of meeting a specified standard. If chemicals can be recovered then the cost of emission control to the industry will be estimated by finding the change in net expenditures attributable to satisfying the emission standards.

Using the multi-path flow diagrams, it is possible to make an analysis of any single source or combination of sources which exist in kraft mills. Thus, an estimate for a single plant can be made by selecting the applicable subset of sources from the multi-path flow diagram.

13.3.3.1 Assumed Performance Standards

The model is designed so that the optimal solution can be specified for various numerical values of performance standards (see Section 13.4.2). In order to obtain a cost estimate for an existing set of standards, the state of Oregon standards have been utilized in this analysis. It should not be concluded, however, that these standards are "typical" or "representative" of practices in other states. They are used in this study only to provide one estimate of emission control costs. The relevant excerpt from these standards is presented below (7).

"EMISSION LIMITATIONS. The following emission limits are based upon average daily emissions.

(1) Emission of TRS.

(a) The emission of TRS from a recovery furnace stack shall not exceed 2 pounds of sulfur per ton of equivalent air-dried kraft pulp or 70 ppm expressed as H_2S on a dry gas basis, whichever is the more restrictive.

(b) No later than July 1, 1975, the emission of TRS from the recovery furnace stack shall not exceed 0.5 pound of sulfur per ton of equivalent air-dried kraft pulp or 17.5 ppm, expressed as H_2S on a dry gas basis, whichever is the more restrictive, or such other limit of TRS that proves to be reasonably attainable utilizing the latest in design of recovery furnace equipment, controls and procedures.

(c) No later than July 1, 1972, the emission of noncondensibles from digesters and multiple effect evaporators shall be treated to reduce the emission of TRS equal to the reduction achieved by thermal oxidation in a lime kiln.

(2) Emission of Particulate Matter.

(a) No later than July 1, 1975, the emissions of particulate matter from the recovery furnace stack shall not exceed 4 pounds per ton of equivalent air-dried kraft pulp.

(b) No later than July 1, 1975, the emission of particulate matter from lime kilns shall not exceed 1 pound per ton of equivalent air-dried kraft pulp.

(c) No later than July 1, 1972, the emission of particulate matter from the smelt tank shall not exceed 1/2 pound per ton of equivalent air-dried kraft pulp."

It is seen that the standards can be classified as equiproportional, so that from the point of view of the standards, each source is independent.

Using the Oregon standards as a data source, the allowable particulate emission from source 7 in a kraft mill is calculated as follows:

B = 500 tons of pulp/day,

$\bar{a}_i^{(k)} = \bar{a}_7^{(1)}$ = 4 lbs. of particulates/ton of pulp, so that

$\bar{a}_7^{(1)}(B)$ = 4(500)/2000 = 1.0 tons of particulates/day.

13.3.3.2 Assumed Emissions

The assumed unit emissions ($a_i^{(k)}$) for a 300, 500, and 1000 ton/day pulp mill were obtained from Table 13-1. It is desired to calculate $a_i^{(k)}B$, the right hand side of Eq. 13.3. Sample calculations are shown below.

B = 500 tons of pulp/day,

$a_i^{(k)} = a_7^{(1)}$ = 140 lbs. of particulates/ton of pulp, so that

$a_7^{(1)}B$ = 140(500)/2000 = 35.0 tons of particulates/day.

13.3.3.3 Control Bounds

It is necessary to know how much a given control can remove at a specified source and what the unit removal costs are. The upper bound on the actual removal capability, $\bar{Y}_{ijl}^{(k)}$, was estimated using the annual operating efficiency estimates from Chapter 5. For precipitators, five removal ranges (expressed as percentages) were considered: 0-89.5, 89.5 - 94.5, 94.5 - 98.5, 98.5 - 99.0, and 99.0 - 99.5. Thus

$$\bar{\gamma}_{ij1}^{(k)} = \bar{\gamma}_{711}^{(1)} = .895 - 0 = 0.895$$

$$\bar{\gamma}_{ij2}^{(k)} = \bar{\gamma}_{712}^{(1)} = .945 - .895 = 0.05$$

$$\bar{\gamma}_{ij3}^{(k)} = \bar{\gamma}_{713}^{(1)} = .985 - .945 = 0.04$$

$$\bar{\gamma}_{ij4}^{(k)} = \bar{\gamma}_{714}^{(1)} = .990 - .985 = 0.005$$

$$\bar{\gamma}_{ij5}^{(k)} = \bar{\gamma}_{715}^{(1)} = .995 - .990 = 0.005$$

The control bounds for each removal range, $a_i^{(k)}(B)\ \bar{\gamma}_{ij1}^{(k)}$, may then be calculated. From the previous section, $a_7^{(1)}\ B = 35.0$. Thus, the control bounds for a precipitator at source 7 can be calculated as follows:

$\bar{\gamma}_{711}^{(1)}\ (a_7^{(1)}B)$ = 0.895(35) = 31.25 tons of part./day.

$\bar{\gamma}_{712}^{(1)}$ (") = 0.05 (35) = 1.75 tons of part./day.

$\bar{\gamma}_{713}^{(1)}$ (") = 0.04 (35) = 1.40 tons of part./day.

$\bar{\gamma}_{714}^{(1)}$ (") = 0.005 (35) = 0.175 tons of part./day.

$\bar{\gamma}_{715}^{(1)}$ (") = 0.005 (35) = 0.175 tons of part./day.

13.3.3.4 Unit Control Cost Analysis - Case I

The Case I cost analysis is applicable for either:

1. A new mill making its initial investment decision in control equipment; or
2. An existing mill which is replacing obsolete equipment. This obsolescence, however, did not result from emission limitations imposed by control agencies.

The fixed cost of a precipitator at source 7, and at all other sources, can be obtained using the procedure described in Section 13.3.1. Knowing the variable costs of emission control over a specified range of control and the amount of emissions which can be removed, the variable costs, $c_{ijl}^{(k)}$, can be determined. A sample calculation for a Case I investment is presented in Table 13-4.

This cost analysis would not be appropriate for examining an existing mill which is required to make an additional investment in control equipment due to the imposition of emission standards. The latter situation may be viewed as causing premature obsolescence of existing equipment. It is not possible to generalize about the present value of this existing equipment for all mills without a detailed study on a mill by mill basis.

13.3.3.5 Unit Control Cost Analysis - Case II

The emission standards would have a relatively severe cost impact on a mill which has just recently installed control equipment without cognizance of impending emission standards which might necessitate modifying or replacing this relatively new equipment. This case (II) will be analyzed as the other limiting condition to consider so that the range of cost impact for any mill (existing or planned) might be determined.

13.3.3.5.1 Add-On Particulate Controls at Recovery Boiler

If a mill has an existing control device in operation, the costs and revenues from this investment are historical or sunk expenditures; i.e., will not be affected by the decision to add-on additional equipment. What is affected most significantly is the particulate removal which can be achieved by this add-on equipment.

TABLE 13-4

SAMPLE CALCULATION OF INCREMENTAL COSTS FOR PRECIPITATORS - CASE I ANALYSIS (i = 0.10)

SOURCE 7 of a 500 ADT/DAY MILL

(1) Removal Range: %	(2) Total Incremental Cost $/Day	(3) Particulates Removed: Tons/Day	(4) Unit Incremental Cost/Ton $/Ton = Col.(2) ÷ Col.(3)	(5) Symbol
0-89.5	$366.00	31.25	$11.70	$c_{711}^{(1)}$
89.5-94.5	49.70	1.75	28.40	$c_{712}^{(1)}$
94.5-98.5	73.80	1.40	52.80	$c_{713}^{(1)}$
98.5-99.0	35.80	0.175	205.00	$c_{714}^{(1)}$
99.0-99.5	86.80	0.175	495.00	$c_{715}^{(1}$

For the sample analysis shown in Table 13-4 the decision-maker decides to recover between 0 and 99.5 percent of the 35 tons of chemicals. However, given that he has an existing 90 percent precipitator (with an assumed AOE of 89.5 percent) the decision-maker must decide how much to recover of the remaining 3.675 tons of chemicals that leave the existing 90 percent precipitator. The corresponding sample calculations for this situation are shown in Table 13-5.

TABLE 13-5

SAMPLE CALCULATIONS OF INCREMENTAL COSTS FOR ADDITIONAL PRECIPITATOR - CASE II ANALYSIS
(i = 0.10)

SOURCE 7 OF A 500 ADT/DAY MILL

(1) Removal Range For Additional Particulates %	(2) Total Incremental Cost $/Day	(3) Additional Particulates Removed Tons/Day	(4) Unit Incremental Cost/Ton = Col.(2) ÷ Col.(3)
0 - 89.5	$366.00	3.28	$ 112.00
89.5 - 94.5	49.70	0.184	270.00
94.5 - 98.5	73.80	0.147	502.00
98.5 - 99.0	35.80	0.018	1990.00
99.0 - 99.5	86.80	0.018	4820.00

Comparison of Tables 13-4 and 13-5 reveals that the total incremental costs stay the same. However, the amount of particulates removed by the add-on precipitator in each removal range is nearly an order of magnitude less. Correspondingly, the unit incremental removal cost/ton increases significantly. Thus for this configuration it is apparent that a single larger precipitator is more economical than two smaller units in series. For example, the average unit incremental costs in the 89.5 - 98.5 percent range are about $39/ton for a single larger unit as compared to adding an additional 89.5 percent unit at a unit cost of $112/ton for a similar removal range.

If a decision is made to replace an existing control then the operating costs associated with this control fall to zero. The unamortized capital costs, however, continue at their same level for the remainder of the amortization period. Thus the problem in this case is to determine the net expenditure required to replace the existing control with an acceptable alternative.

13.3.3.6 Value of Recovered Chemicals

The value of recovered chemicals varies from mill to mill depending on local conditions. For this analysis a value of \$30/ton has been selected as a realistic estimate for the recovery boiler and smelt tank. A value of \$15/ton has been used for the lime kiln. The effect of varying these assumed values will be evaluated later in this chapter.

13.3.3.7 Results of Analysis of Particulate Emissions for Case I.

This section describes the results from applying the mathematical model to analyzing particulate emissions. The multipath flow diagram for particulates indicates particulate emissions from the following sources: [6, 7, 11, 12, 15, 16, 17, 18, 20, 21, 22, 23, 24, 25, 26]. However, the particulate emissions from the slake tank are unknown so that it will not be possible to analyze this source (No. 22). Results from analysis of each of the other sources is presented below.

Detailed analysis of the problem revealed that it is possible to decompose this single large optimization problem into equivalent sub-problems. While commodity interrelationships are felt to exist in the pulp industry, no one was able to quantify this interrelationship so that $\rho_{ijl}^{(k'k)} = 0$ for all k in Eq. 13.3. The Oregon standards may be classed in the equiproportional abatement category so that each source can be analyzed independently of other sources. With the problem decomposed in this manner, the problem of analyzing the integer variables may be resolved by explicit enumeration of the remaining alternatives.

In the absence of performance standards, the industry is assumed to be making a straightforward investment decision of choosing the optimal control and removal efficiency Given the answers to this problem, the performance standard is added as an additional constraint, and its impact is thereby evaluated.

Lastly, to examine the case of existing mills with usable control equipment, the above analysis can be repeated with the additional constraint that the cost of upgrading or replacing this equipment be included in the analysis. Such an analysis will be made later for an existing mill.

The results of the cost impact studies for the recovery boiler sources are shown in Table 13-6. For source 6 of a 500 ton/day mill, the results indicate that the performance standard reduces net revenues from $333/day to $315.40. Thus, the reduction in net revenue attributable to satisfying the performance standard is $17.60/day. The low yield source (No. 7) derives larger net revenues than the high yield source (No. 6). However, the reduction in net revenue from satisfying the emission standard at source 7 is also seen to be greater than for source 6 for this mill size. Thus for sources 6, 7, 11, and 12, it appears that emission control equipment is an attractive investment and that the selected standards do not have a significant impact on the investment decision. Case I removal in the 90 percent range was selected for the smaller mill sizes while 95 percent was selected for the 1000-ton mill size. No significant economies or diseconomies of scale were evident.

T A B L E 13-6

ANALYSIS OF PARTICULATE EMISSIONS FROM RECOVERY BOILERS

CASE I
(i = 0.10)

Source	Mill Size Tons/Day	Air Flow 1000 CFM	Particulates Tons/Day	Optimal Soln:Net Revenue: $/Day W/O Stds.	Optimal Soln:Net Revenue: $/Day W. Stds.	Cost of Meeting Stds. $/Day
6 or 11	300	58	13.9	148.00	125.50	22.50
	500	97	23.2	333.00	315.40	17.60
	1000	194	46.5	815.00	796.50	18.50
7 or 12	300	88	21.0	290.00	263.30	26.70
	500	146	35.0	571.00	547.00	24.00
	1000	292	70.0	1301.00	1245.00	56.00
15 or 17	300	52.5	4.5	0	-89.00	89.00
	500	87.5	7.5	0	-66.20	66.20
	1000	175	15.0	0	-23.60	23.60
16 or 18	300	79	6.8	0	-96.20	96.20
	500	131	11.3	0	-68.00	68.00
	1000	262	22.5	56.80	- 9.20	66.00
20	300	84	31.5	582.00	564.00	18.00
	500	139	52.5	1075.00	1056.00	19.00
	1000	278	105.0	2320.00	2285.00	35.00

The analysis of source 15 (and equivalent source 17) and source 16 (and equivalent source 18) indicates that there is a positive cost of meeting the standards for all mill sizes. A removal efficiency in the range of 90 percent, based solely on optimum economic considerations with a gross return on investment of 10 percent, was found for these sources. A small positive cost of meeting the standards was found for source 20. A removal efficiency in the range of 95 percent, based solely on optimum economic considerations with a gross return on investment of 10 percent, was observed for this source.

The results for the smelt tank (source 21) indicate a net cost incurred to satisfy the performance standards as shown in Table 13-7. Without the standard, the mesh pad offers an economically attractive but low removal efficiency alternative so that a positive net revenue results. Imposition of the standard necessitates the use of a different control with a higher unit cost so that a positive net cost results. A removal efficiency in the range of about 75 percent was observed for this source based solely on optimum economic considerations with a gross return on investment of 10 percent.

A similar analysis of the lime kiln selected indicated a removal efficiency of about 99 percent of the particulates so that the standard of constraint is not binding. Particulate emission control at lime kilns appears to be an attractive investment based on this Case I analysis.

13.3.4 LIMITATIONS OF THE MODEL

The optimization model provides the best solution to the problem for the assumed set of conditions. The results would be more accurate if the input emission data, cost data, et cetera, are calculated for a specific plant. This study has focused on the behavior of hypothetical pulp mills in the United States. The intent of the study is to provide an analysis, based on the best available data, of the expenditures for emission control in this industry. The results of analyses for such hypothetical mills are not to be considered applicable to any specific pulping operation in this country.

Improvements in this concept will undoubtedly be possible with further study and experience gained with collection and processing of data. This may warrant changes in the preceding formulations and models or constraints.

T A B L E 13-7

ANALYSIS OF PARTICULATE EMISSIONS FROM SMELT TANK (#21) and LIME KILN (#23-#26)

CASE I
(i = 0.10)

Source	Mill Size Tons/Day	Air Flow 1000 CFM	Particulates Tons/Day	Optimal Soln:Net Revenue: $/Day W/O Stds.	Optimal Soln:Net Revenue: $/Day W. Stds.	Cost of Meeting Standards $/Day
21	300	9.4	0.6	2.60	-19.40	22.00
	500	15.6	1.0	10.20	-14.00	24.20
	1000	31.2	2.0	31.60	- 7.00	38.60
23 or 25	300	6.5	5.85	66.00	66.00	0
	500	10.9	9.75	120.00	120.00	0
	1000	21.8	19.50	251.00	251.00	0
24 or 26	300	8.5	7.65	92.00	92.00	0
	500	14.2	12.75	166.00	166.00	0
	1000	28.4	25.5	321.00	321.00	0

13.4 ASSIGNMENT OF PARTICULATE CONTROL COSTS (PROCESS OR EMISSION CONTROL) - CASE I

An evaluation of the impact of performance standards on particulate emission control decisions was presented in the previous section for a single set of standards and a single value of recovered chemicals. It is often desired to evaluate the effect on the optimal solution of changes in some of the original assumptions. Sensitivity analysis is a post-optimal procedure which permits examination of the response of the optimal solution to changes in the assumed conditions. Control of SO_2 and total organics takes place only when required by the performance standards. Consequently, the total expenditure is chargeable to satisfying the performance standards. However, the cost of particulate control can often be reduced significantly because of the value of the recovered chemicals. Thus the following post-optimal analyses for the particulate sources will be presented for Case I. The other case of an existing mill adding on additional control devices in response to new performance standards is not considered here.

1. For each source, how high must the value of the recovered chemicals be in order to justify emission control solely for chemical recovery?
2. For each source, at what value of recovered chemicals would the optimal emission control not be employed in the absence of the performance standard for each source?
3. For each source, what is the effect of changing performance standards?
4. For each source, what is the effect of using a rate of return (before taxes) of 20 percent instead of 10 percent.

13.4.1 EFFECT OF VALUE OF RECOVERED CHEMICALS - Case I

This section examines the value of recovered chemicals needed to justify particulate removals greater than would be required by the performance standard. Thus, if the performance standard constraint was initially binding, there is some higher value of recovered chemicals at which the constraint would not be binding and the decision-maker would rationally remove more particulates than he is required by the standard.

The second item examined in this section is the effect of decreasing the value of recovered chemicals to the point that a rational decision-maker would elect not to use the control he originally selected.

The results of this analysis are presented in Table 13-8. For 500 ton per day pulp mills, it is seen that emission control for chemical recovery only can be justified for recovery boilers if the value of chemicals is in the $40 to $240 range. The required value for the smelt tank is $46 while the required value for lime kilns is only $7 to $10. It is also apparent that the optimal control (at some lower percent removal) would be selected for recovery boilers in 500 ton/day mills if the unit value of chemicals is in the $8 to $40 range.

No sensitivity analysis was made of the other case where additional particulate controls at an existing mill must be added to satisfy a newly imposed standard.

13.4.2 EFFECT OF VARYING PERFORMANCE STANDARDS-CASE I

This section analyzes the impact of changing particulate performance standards on the optimal solution. Insights can be gained by examining the total cost function over the feasible removal range. This analysis was performed for each source. For the controls examined, the marginal cost (as a function of quantity of particulates removed) increases in the higher removal range. Thus, removal of the last units of particulates is the most expensive for a given control. Another factor which increases costs is when a change in

TABLE 13-8

EFFECT OF VALUE OF RECOVERED CHEMICALS ON PARTICULATE CONTROLS

CASE I ANALYSIS
(i=0.10)

Source	Value of Recovered Chem. To Justify Process Control Beyond Standards: $/Ton			Value of Recovered Chem. To Justify Using Any Optimal Control: $/Ton		
	300 T/D	500 T/D	1000 T/D	300 T/D	500 T/D	1000 T/D
6	$ 55.00	$ 52.70	$ 53.30	$ 18.10	$ 13.90	$ 10.70
7	52.50	52.80	55.30	14.50	11.80	9.65
11	55.00	52.70	53.30	18.10	13.90	10.70
12	52.50	52.80	55.30	14.50	11.80	9.65
15	52.80	40.20	30.80	52.80	40.20	30.80
16	269.00	240.00	194.00	37.80	30.40	24.90
17	52.80	40.20	30.80	52.80	40.20	30.80
18	269.00	240.00	194.00	37.80	30.40	24.90
20	247.00	204.00	170.00	9.40	7.60	6.10
21	67.00	46.00	34.00	67.00	46.00	34.00
23	12.60	9.50	7.00	12.60	9.50	7.00
24	9.60	7.20	5.30	9.60	7.20	5.30

the selected control must be made because the previously selected control has reached its maximum removal capability. Both of those factors will be analyzed.

The analysis of the control cost function for recovery boiler sources is shown in Table 13-9. The results are presented for the entire range over which controls are feasible. For source 7, control 1 can be employed in the 0-89.5 percent range; control 1 alone, or 1 and 2, or 1 and 6 in the 89.5-98.5 percent range; and only control 1 in the 98.5 to 99.5 percent range. The next column shows the least cost control to select. Examination of the variable cost, in $/ton, indicates the cost functions are convex and that the marginal cost of particulate removals in the upper ranges is relatively high. For source 7, the marginal costs are $28.40/ton in the 89.5 to 94.5 percent range whereas they rise to almost $500/ton in the 99.0-99.5 percent range.

Analysis of the lime kiln and the smelt tank indicates high marginal cost for lime kilns above 99 percent removal, and increasing costs due to changing controls for the smelt tank as shown in Table 13-10.

TABLE 13-9

ANALYSIS OF COST FUNCTION FOR VARYING PERCENT REMOVALS FOR RECOVERY BOILERS IN 500 TON/DAY MILL

CASE I
(i = 0.10)

Source	Performance Standard Proportion Removed (AOE)	Feasible Control Numbers	Selected Control Number	Fixed Cost $/Day	Variable Cost $/Ton	Particulates Removed Tons	Addnl. Fixed Cost $/Day	Total Cost $/Day
6 or 11	0-.895	1	1	256.00	1.50	20.8	-	287.00
	.895-.945	1 1&2 1&6	1		38.50	1.16		332.00
	.945-.985	1 1&2 1&6	1		52.70	.93	-	381.00
	.985-.990	1	1	-	336.00	.116	-	420.00
	.990-995	1	1	-	472.00	.116	-	475.00
7 or 12	0-.895	1	1	329.00	1.18	31.3	-	366.00
	.895-.945	1 1&2 1&6	1	-	28.40	1.75	-	416.00
	.945-.985	1 1&2 1&6	1	-	52.80	1.4	-	490.00
	.985-.990	1	1	-	205.00	.175	-	526.00
	.990-.995	1	1	-	483.00	.175	-	611.00

TABLE 13-9 (continued)

15 or 17	0-.895	1	1	241.00	4.32	6.72	-	270.00
	.895-.985	1&6	1&6	-	258.00	.675	-	444.00
	.985-.990	1&6 7	1&6	-	264.00	.038	-	454.00
	.990-.994	1&6 7	1&6	-	867.00	.030	-	480.00
16 or 18	0-.895	1	1	306.00	7.10	10.1	-	378.00
	.895-.985	1&6	1&6	-	238.00	1.02	-	620.00
	.985-.990	1&6 7	1&6	-	268.00	.056	-	635.00
	.990-.994	1&6 7	1&6	-	1130.00	.045	-	686.00
20	0-.895	1	1	318.00	0.76	47.0	-	354.00
	.895-.945	1 1&2 1&6	1	-	18.70	2.62	-	403.00
	.945-.985	1 1&2 1&6	1	-	34.20	2.10	-	475.00
	.985-.990	1	1	-	134.00	.26	-	510.00
	.990-.995	1	1	-	333.00	.26	-	596.00

TABLE 13-10

ANALYSIS OF COST FUNCTION FOR VARYING PERCENT REMOVALS FOR SMELT TANK AND LIME KILN IN 500 TON/DAY MILL

CASE I
(i = 0.10)

Source	Performance Standard Proportion Removed (AOE)	Feasible Control Numbers	Selected Control Number	Fixed Cost $/Day	Variable Cost $/Ton	Particulates Removed Tons	Addnl. Fixed Cost $/Day	Total Cost $/Day
21	0 - .75	6,8,9	9	9.00	4.00	.75	-	12.00
	.75- .90	6,8	8	-	10.00	.15	27.50	41.00
	.90- .97	6	6	-	26.00	.07	12.50	55.00
23 or 25	0 - .99	6	6	24.00	7.00	9.65	-	91.00
	.99- .999	6	6	-	860.00	.01	-	100.00
24 or 26	0 - .99	6	6	24.00	5.40	12.60	-	92.00
	.99- .999	6	6	-	656.00	.013	-	100.00

13.4.3 EFFECT OF USING HIGHER RATE OF RETURN

This section analyzes the impact of using a 20 percent instead of a 10 percent rate of return. These are gross rates of return and do not include deductions for taxes. The 10 percent rate of return was used in this study in order to be compatible with previous industrial studies of NAPCA. The 20 percent rate of return is an estimate by pulping industry representatives of their minimum required rate of return.

This analysis will be done for the particulate control devices in 500 TPD mills and the results will be compared with the 10 percent rate of return analysis. The results of this analysis are shown in Table 13-11.

The use of a higher rate of return will necessarily decrease the amount of surplus revenue relative to that rate of return. This effect is shown by comparing columns two and five. The use of a higher rate of return had the expected result of significantly reducing net revenues. The cost of satisfying the standards increased significantly. Also, cost increases significantly or accordingly, as in Table 13-11.

13.5 TRENDS IN FUTURE CAPITAL EXPENDITURES

Looking to the future the pulping industry is faced with two parallel problems in meeting emission standards. One problem is that of upgrading existing facilities; the other is to assure compliance of new mills or mill expansions which must be built to satisfy the increasing demand for wood pulp.

The following sections present example emission control cost calculations for a 500 TPD new mill and an identical size existing mill.

TABLE 13-11

EFFECT OF RATE OF RETURN ON OPTIMAL SOLUTION FOR CASE I ANALYSIS OF PARTICULATE CONTROLS: 500 TPD MILL

	i = 0.10			i = 0.20		
Source	Optimal Solution Net Revenue:$/Day		Cost Of Meeting Stds. $/Day	Optimal Solution Net Revenue:$/Day		Cost Of Meeting Stds.
	W/O Stds.	W. Stds.		W/O Stds.	W. Stds.	
6 or 11	333.00	315.40	17.60	255.00	220.90	34.10
7 or 12	571.00	547.00	24.00	465.00	418.30	46.70
15 or 17	0	-66.20	66.20	0	-142.00	142.00
16 or 18	0	-68.00	68.00	0	-166.00	166.00
20	1075.00	1056.00	19.00	520.00	411.00	109.00
21	10.20	-14.00	24.20	7.30	-23.30	30.60
23 or 25	120.00	120.00	0	33.80	33.80	0
24 or 26	166.00	166.00	0	80.00	80.00	0

13.5.1 EXAMPLE CALCULATIONS FOR NEW MILL

This section shows an example for a new 500 TPD mill with the following configuration:

Continuous digestion
High or low yield
High solids evaporation
Incineration in lime kiln

The controls employed should be sufficient to meet 1975 Oregon standards. Referring to the multi-path flow diagram, this example mill has the following set of sources [1, 4, 19, 20, 21, 22, 25, 26]. Analysis of particulates, H_2S, SO_2, and organic sulfur compounds is shown below. The analysis of power boilers is not included in this study. Emission control at that source is a total cost since no revenues are derived from recovered chemicals.

13.5.1.1 Particulate Controls - New Mill

The sources of particulates for this configuration are obtained from Figure 13-2, the multi-path flow diagram, and comprise the following subset of sources [20, 21, 22, 25, 26]. From Table 13-6, the cost of meeting the standards is obtained and is presented below.

TABLE 13-12

PARTICULATE EMISSION CONTROL COST ANALYSIS-NEW 500 TPD MILL

Source	Cost of Meeting Stds. $/Day
20	$19.00
21	24.20
22	-*
25 or	0
26	0

Daily Cost of Meeting Standards

High Yield	$43.20
Low Yield	43.20

*No unit particulate emission could be estimated. It appears that net revenue would be about zero so analysis will be done using this assumption.

13.5.1.2 H_2S and Organic Sulfur Compounds - New Mills

The sources of these emissions are shown in Figure 13-3 and are the subset [1, 4, 21, 25, 26]. Using the fact that the standards specify treatment equivalent to incineration in a lime kiln, the control cost is \$37.20/day, for H_2S and organic sulfur compounds.

13.5.1.3 SO_2 Control - New Mills

The sources of SO_2 emissions are shown in Figure 13-4 and are the subset [4, 25, 26]. The multi-path diagram indicates no known SO_2 controls so that the control cost is zero.

13.5.2 EXAMPLE CALCULATIONS FOR AN EXISTING MILL

This section shows an example for an existing 500 TPD mill with the following configuration:

Batch digestion
High or low yield
Direct contact evaporation
No incineration in lime kiln
No black liquor oxidation

The controls employed should be sufficient to meet 1975 Oregon standards. Referring to Figure 13-1, this example has the following set of sources [1, 2, 3, 5, 6, 7, 21, 22, 23, 24]. Analysis of particulates, H_2S, SO_2, and organic sulfur compounds is shown below. This analysis provides an estimate of the initial cost impact of emission standards on such mills. However, this impact is not permanent. It represents a measure of the cost of prematurely replacing existing equipment. The analysis of power boilers is not included in this study. Emission control at that source is a total cost since no revenues are derived from recovered chemicals.

13.5.2.1 Particulate Controls - Existing Mill

The sources of particulates for this configuration are obtained from Figure 13-2 and comprise the following subset of sources [6, 7, 21, 22, 23, 24]. It is assumed that the mill has the following control equipment already in use.

1. 90 percent precipitator at sources 6, 7
2. Mesh pad at source 21
3. 80 percent scrubber at sources 23, 24

This equipment is assumed to have useful service life remaining and credits will be given accordingly. The least cost way to upgrade to meet the standards will be selected. For sources 6 and 7, an 80 percent cyclonic scrubber can be added to satisfy standards. For source 21, the mesh pad will be replaced by a packed tower scrubber. For sources 23 and 24, the 80 percent scrubber will be replaced by a 99 percent venturi scrubber. The results of this analysis for each applicable source of particulates are shown in Table 13-13. It is apparent that particulate emission standards exert a strong impact on costs for existing mills which must upgrade to satisfy new standards. It is not possible to know directly what net revenues were without the standards for this case. Thus, the cost of meeting the standard is not known. For example, though a positive net revenue is shown for sources 23 and 24, it cannot be concluded that the industry would voluntarily invest at this level because the original control level may have yielded an even larger net revenue.

13.5.2.2 H_2S and Organic Sulfur Compounds

The sources of these emissions are shown in Figure 13-3 and are the subset [1, 2, 3, 5, 6, 7, 21, 23, 24]. In order to satisfy the standards, it is necessary to add lime kiln incineration (at a cost of $37.20/day) and weak black liquor oxidation (at a cost of $264/day).

13.5.2.3 SO_2 Control

The sources of SO_2 are shown in Figure 13-4 and are the subset [2, 3, 5, 6, 7, 23, 24]. The multi-path diagram indicates no known SO_2 controls so that the control cost is zero.

T A B L E 13-13

PARTICULATE EMISSION CONTROL COST ANALYSIS - EXISTING MILL

Source	Net Revenue W. Stds. $/Day
6 or	- $124.00
7	- 113.00
21	23.00
22	-*
23 or	13.50
24	57.00

Total Net Revenue w. Stds.

High Yield	-$133.50
Low Yield	- 79.00

*No unit particulate emission could be estimated. Assumed that net revenue was zero.

13.5.3 CONTROL EXPENDITURES AT NEW MILLS

Kraft Flow Sheet No. 10 (Chapter 3) depicts an approach to the control of new facilities incorporating control options which have been shown to be effective and practical. This approach emphasizes the use of a process change to reduce emissions from the recovery boiler, provides for lime kiln incineration of non-condensible gases, and calls for high efficiency scrubbers to be installed on the lime kiln, smelt tank, and slaker tank. BLO is not required because of the process change involving the recovery boiler. The only source uncontrolled by this scheme is the pulp washers. Even this source might eventually be controlled by the use of diffusion or pressure washing as described in Chapter 6.

The single most significant innovation on Kraft Flow Sheet No. 10 is the utilization of the new high solids evaporator to supplant the more conventional DC evaporator or Venturi evaporator/scrubber systems. Figures 5-46 and 5-47 reflect cost data which allow for a comparison of the total capital cost for the "new" recovery system with the total capital cost of the conventional recovery system. This comparison suggests that the capital cost of the "new" system is only slightly higher (within 10 percent) than the capital cost of the conventional system. When the annual costs of the two systems are compared, however, preliminary estimate of costs for the "new" system come out lower than those of the conventional system for a rate of return equal to 10 percent.

It seems reasonable to conclude, therefore, that new mills and mill expansions can be effectively controlled and that the costs for using "new" recovery systems do not differ drastically from the cost of the more conventional designs.

The cost impact analysis presented previously suggests that standards for particulate emission as proposed by the states of Washington and Oregon for 1975 would not cause a significant departure from the particulate control level that would be selected in their absence (For i = 0.10). However, should the standards become more stringent than currently envisioned, the analysis shows that marginal costs of satisfying more stringent standards are significantly higher than the anticipated value of the recovered chemicals.

Prior analysis has shown that a proper measure of control effectiveness for H_2S and other organic sulfur compounds defies description. With standards specifying that treatment shall be "equivalent" to lime kiln incineration, we reach a point where the decision is either go or no go. There is no economic incentive to make an investment in H_2S and organic sulfur control so that the costs may be viewed as directly attributable to pollution control.

13.5.4 CONTROL EXPENDITURES AT EXISTING MILLS

The problem of what to do with an existing mill to bring it into compliance with standards similar to those promulgated in the Pacific Northwest has been the subject of much debate during the course of this study. While a firm consensus has not been reached, the tenor of the debate has been that the control of H_2S and other organic sulfur compounds emanating from recovery boilers can be achieved to a degree through the use of 99+ percent black liquor oxidation or by the conversion of existing fairly modern units to incorporate one of the new high solids evaporator designs. It is conceivable though that for some older recovery systems, the odorous emissions may never be reduced to levels which are currently being considered by regulatory authorities, even though the most modern technology is employed. This means that these older recovery systems may have to be scrapped and replaced with a new system which eliminates direct contact between the flue gas and black liquor.

The impact of standards for the H_2S emissions from recovery boilers could be dramatic. Apparently, there is a consensus that standards set for 1972 (in Washington and Oregon) can be met by the utilization of BLO or by conversion to one of the "new" design evaporator systems. Standards proposed for 1975, however, might only be met by scrapping existing process equipment and replacing it with a completely new system which eliminates direct contact between the flue gas and black liquor.

If BLO can be utilized effectively, or if a conversion of existing facilities can be successfully achieved, then the capital costs (for a 500 TPD mill) could range from $200,000 (for BLO) to $1.5 million (for an air contact evaporator). If it is determined, however, that a new recovery boiler, per se, is required, then the capital costs could approach $8 million.

13.6 REFERENCES

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